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Vibronic coupling at a chromium ion in a trigonal field in GaAs

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Résumé. — Nous présentons ici les résultats préliminaires des calculs que nous avons effectués sur le système $\text{Cr}^{2+}\text{-X}$ (raies à 0,839 eV) dans GaAs. La structure à champ nul de ces raies ne peut être expliquée qu'à la condition d'introduire un champ trigonal fort. Les principaux points qui sont expliqués uniquement par cette forte valeur sont : la réduction de l'énergie Jahn-Teller et l'existence de raies vibroniques notées I et J. Un Hamiltonien de spin est présenté qui permet de décrire la structure fine à champ nul ainsi que les intensités de raies.

Abstract. — We present here the preliminary results of our calculations on the $\text{Cr}^{2+}\text{-X}$ (0.839 eV lines) system in GaAs. These calculations show that it is necessary, in order to explain the zero field splitting, to introduce a strong trigonal field. The main points that are explained by the presence of a strong trigonal field are the reduction of the Jahn-Teller energy and the occurrence of vibronic lines labelled I and J. A spin Hamiltonian is also presented that explains the zero field fine structure and the line intensities.

The chromium related luminescence lines at 0.839 eV in GaAs were originally interpreted as an internal transition (${}^5\text{E} \rightarrow {}^5\text{T}_2$) of an isolated Cr^{2+} ion. This interpretation has subsequently been shown to be incorrect [1-3]. White [1] proposed a model where the transition would be an exciton recombination at a chromium ion with C_{3v} symmetry. In a previous paper [4], hereafter referred to as paper I, we presented a model based on the analysis of the zero phonon fine structure [5] that gave the main characteristics of the centre. These characteristics are, at the present time, still in agreement with experimental results. These are :

- 1) internal transition of a chromium ion in C_{3v} symmetry (${}^5\text{E}^* \rightarrow {}^5\text{E}$);
- 2) the ${}^5\text{E}$ ground state comes from a ${}^5\text{T}_2$ state of T_d symmetry ;
- 3) the ground state Jahn-Teller energy is ~ 20 meV ($2.2 \hbar\omega$) [4] and is due to the coupling with an ε trigonal mode ;
- 4) the fine structure of the ${}^5\text{E}^*$ state is well described in the framework of static crystal field, and
- 5) this model corresponds to two possible microscopic defects : either a Cr^{2+} ion on a gallium site coupled with a positively charged impurity or defect on an arsenic site, or a Cr^0 interstitial coupled to a negatively charged impurity.

We consider that the first defect ($\text{Cr}^{2+}\text{-X}$) is the only possibility. The first reason is that recent calculations by Deleo *et al.* [6] showed that the crystal field splitting of interstitial chromium (Cr^0) in silicon should be very weak. It seems very likely that the same would be true for Cr^0 in GaAs, since a $\text{Cr}^{2+}\text{-X}$ defect should have a crystal field splitting close to that for isolated Cr^{2+} (~ 0.839 eV

compared to ~ 0.820 eV). Secondly, the position of the energy level associated with the ground state of $\text{Cr}^{2+}\text{-X}$ (0.6 eV above the valence band [4]) is close to the position of the ground state of Cr^{2+} (0.75 eV above the valence band)* [4]. In this paper we intend to show and explain the similarities and differences between $\text{Cr}^{2+}(\text{T}_d)$ and $\text{Cr}^{2+}\text{-X}(\text{C}_{3v})$.

Eaves *et al.* [7] and Killoran [8] have shown that the symmetry of the centre is indeed trigonal using Zeeman experiments. Further work by Eaves *et al.* [9, 10] confirm our model and show that :

- 1) the transition is $^5\text{E}^* \rightarrow ^5\text{E}$,
- 2) the $^5\text{E}^*$ state can be described by an effective Hamiltonian

$$\lambda \sigma_3 S_3, \quad \text{and}$$

- 3) the ^5E ground state effective Hamiltonian is dominated by the terms :

$$\mu_1 \{ \sigma^+ [S_3 S^-]_+ + \sigma^- [S_3 S^+]_+ \} + dS_3^2$$

where $[A, B]_+ = AB + BA$.

Voillot *et al.* [11] have obtained a better solution of the zero phonon lines having proposed a more precise description of the zero field splitting. They use the same model as us (internal transition of a Cr^{2+} ion in C_{3v} symmetry) but with the important difference that the trigonal field is weak. This leads to the description of the ground state as $\text{T}_2 \otimes \varepsilon$ rather than $\text{E} \otimes \varepsilon$ as in our results. In their model, the trigonal field is completely quenched by the vibronic coupling with the ε mode. Further papers by Voillot *et al.* [12, 13] used that model to interpret the Zeeman experiments and the uniaxial stress splitting. However, some features of the experiments were not explained by the model. These are the occurrence of the I and J vibronic lines, the angular dependence of the Zeeman splitting and the non-linear behaviour of the stress splitting in the [100] direction.

Recently, Barrau *et al.* [14] improved on their experimental technique so as to completely resolve the ground state splitting. This ground state is now shown to be composed of seven lower levels grouped in a ^5E state and three upper levels which are labelled I, and are already described in paper I as vibronic lines ($^5\text{A}_1$ state). There we made the approximation that although the trigonal field (900 cm^{-1}) and the Jahn-Teller energy (200 cm^{-1}) were supposed to be of the same order of magnitude, we introduced the Jahn-Teller coupling as a perturbation on an E state (split from T_2 by the trigonal field).

We have now improved the calculations and by making fewer approximations on the vibronic wavefunctions we can give a correct explanation of all experimental results. The complete calculations will be given in a separate paper, but here we will summarize the main implications of our model. We concentrate on the zero field behaviour and show how completely it can be understood.

1. Description of the vibronic coupling in the ground state ($\text{E} + \text{A}_1$) $\otimes \varepsilon_{\text{trig}}$. — We are dealing with a Cr^{2+} ion in T_d symmetry, subject to a trigonal perturbation induced by a first neighbour impurity or defect [4]. The strength of the trigonal field (W) is, *a priori*, unknown. Thus, different situations depending on the magnitude of W can be considered.

From symmetry considerations, we can write the vibronic Hamiltonian as :

$$H = \left[T + \frac{1}{2} M \omega^2 Q^+ Q^- \right] I + E_0 I + \frac{W}{3} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix} + V \begin{bmatrix} 0 & Q^- & 0 \\ Q^+ & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + V' \begin{bmatrix} 0 & 0 & Q^+ \\ 0 & 0 & Q^- \\ Q^- & Q^+ & 0 \end{bmatrix}. \quad (1)$$

The electronic basis for the T_2 orbital state is $\{|-\rangle, |+\rangle, |0\rangle\}$ where $\{|-\rangle, |+\rangle\}$, $\{Q^-, Q^+\}$ belong to E of C_{3v} and $|0\rangle$ belongs to A_1 of C_{3v} . $V = V'$ only if the following conditions are fulfilled :

i) The vibration modes of the cubic case are not changed upon introduction of the trigonal impurity.

ii) The electronic perturbation only acts in the T_2 subspace.

iii) The centre is only coupled with an ε mode (before introduction of the C_{3v} perturbation).

In other cases, especially if the isolated Cr^{2+} is coupled with a τ_2 mode, $V \neq V'$.

If the trigonal field is zero, we are in the isolated Cr^{2+} case and the ground vibronic state is 5T_2 which is subject to a slow dynamic Jahn-Teller effect (considered as a « static » Jahn-Teller effect). The value of that energy, as estimated by different authors [15-17], is thought to be close to 600 cm^{-1} .

If a weak trigonal field is now introduced ($W < E_{JT}$), we have the situation described by Voillot *et al.* [11]. The trigonal field is completely quenched in the vibronic ground state which keeps its T_2 character. This model explains neither why the Zeeman experiments infer a 5E ground state nor the occurrence of the vibronic lines I and J. In the $T_2 \otimes \varepsilon$ scheme, the first excited vibronic state energy remains at $\hbar\omega$ relative to the 5T_2 ground state.

Fig. 1. — Vibronic levels of a 5T_2 state subject to a trigonal field W and coupled with one vibration mode ε . The coupling coefficients are $V = 1.8$ and $V' = +1.8$ (see equation (1)). The effect of the trigonal field is to reduce the Jahn-Teller energy from $6.5\hbar\omega$ for $W = 0$ to $1.7\hbar\omega$ for $W = 100\hbar\omega$. The corresponding shift of the vibronic levels is $3.8\hbar\omega - 1/2\hbar\omega$. The trigonal field also lifts the degeneracy of the 5T_2 ground state (in 5E and 5A_1) and of the ${}^5T_2 + {}^5T_1$ first excited state (in ${}^5A_2 + {}^5E + {}^5E + {}^5A_1$). This effect is only discernible if W is quite strong.

If the trigonal field is very strong ($W \gg E_{JT}$), we have the description used in paper I. There, it is better to introduce the trigonal perturbation which lifts the degeneracy of the T_2 electronic state into E and A_1 first before introducing the vibronic coupling. If W is very strong compared to E_{JT} , the A_1 and E states are not mixed by the vibronic coupling. In that case, the first excited vibronic state is not $\hbar\omega$ above the vibronic ground state, but closer to $(\hbar\omega)^2/2 E_{JT}$ in the strong coupling limit. Here since E_{JT} is equal to $200\text{ cm}^{-1} = 2.2\hbar\omega$, the first excited state ($A_1 + A_2$) is $0.2\hbar\omega$ above. The next two 5E vibronic states are close together around $\hbar\omega$ (Fig. 2). In paper I, we introduced a non-linear coupling in order to lift the accidental $A_1 A_2$ degeneracy, so that the two lines I and J exist. Rather than introducing a non-linear effect in the $E \otimes \varepsilon$ system, it is more logical to take into account the off-diagonal coupling between the two set of vibronic wavefunctions ($E \otimes \varepsilon$ and $A_1 \otimes \varepsilon$) *via* the Hamiltonian :

$$V'[|0\rangle Q^- \langle +| + |0\rangle Q^+ \langle -| + \text{c.c.}]. \quad (2)$$

Such a model gives a good description of the I and J level with $|V'|/|V| \sim 0.2$.

Fig. 2. — Schematic diagram showing the behaviour of the vibronic levels as a function of the trigonal field W . If $W = 0$ (a), the ground state is 5T_2 and the first excited state is $\hbar\omega$ above it. If W is weak (b), the trigonal field is quenched both in the 5T_2 and in the ${}^5T_1 + {}^5T_2$ states. W has to be strong (c) in order to create the A_1 and A_2 levels that give rise to the vibronic lines I and J. If W is infinite (d), the A_1 and A_2 levels become degenerate.

2. **Jahn-Teller effect at $Cr^{2+}(T_d)$ and $Cr^{2+}-X(C_{3v})$.** — If the trigonal perturbation only acts in the T_2 subspace, it is easy to show that $V = +V' = V_e/2$ where V_e is the coupling constant to the ε cubic mode when $W = 0$. Consequently, in the strong trigonal field limit, we should have :

$$E_{JT}(Cr^{2+}) = 4 E_{JT}(Cr^{2+}-X).$$

If, for the isolated Cr^{2+} , we take $E_{JT} = 60$ meV, we predict $E_{JT} = 15$ meV for $Cr^{2+}-X$. This is in good agreement with the value of 20 meV that we estimated in paper I. In figures 1 and 2, we show the evolution of the vibronic levels energies as a function of the trigonal field strength, obtained by a diagonalization of the vibronic coupling. Two main effects of the trigonal field can be observed. First, a reduction in the Jahn-Teller energy : it is divided by four when the trigonal field is increased from 0 to ∞ . The corresponding shift of the vibronic ground state is $\frac{3}{4} E_{JT} - \frac{1}{2} \hbar\omega$. This explains why the observed Jahn-Teller energy is reduced from 600 cm^{-1} (Cr^{2+}) to 200 cm^{-1} for $Cr^{2+}-X$. Second, the vibronic ground state 5T_2 and the first excited state ${}^5T_2 + {}^5T_1$ are split by the introduction of the trigonal field. A_1 and A_2 levels are formed which become degenerate when $W \rightarrow \infty$. These levels give rise to the I and J lines. They are not formed unless W is strong enough.

Thus, we have shown that a finite trigonal field (that is to say of strength at least comparable to the Jahn-Teller energy) had to be introduced to explain the 0.839 eV lines : the occurrence of the I and J vibronic lines and the reduction of the Jahn-Teller energy.

3. **Description of the 5E ground state fine structure and transition probabilities.** — In order to describe the fine structure of the ground state, we can write an effective Hamiltonian on the basis of symmetry considerations.

$$H = \lambda \sigma_3 S_3 + d S_z^2 + \mu_1 \{ \sigma^- [S_3 S^+] + \sigma^+ [S_3 S^-] \} + \mu_2 \{ \sigma^+ S^{+2} + \sigma^- S^{-2} \} \quad (3)$$

Fig. 3. — Best fit of the fine structure of the 0.839 eV line. The experimental data is taken from Barrau *et al.* [14]. The fit is shown by the bars superimposed on the spectrum. The bar positions are given by solving the Hamiltonian (3) for the following values : $\mu_1 = -0.055$ meV, $\mu_2 = 0.01$ meV, $d = -0.07$ meV, $\lambda = 0$. The bar height is given by the transition probabilities that we have calculated (presented in the text). The fitting parameter is the ratio between the A_3 and $A_1(A_2 A_6 A_7)$ intensities. This parameter cannot be calculated *a priori*.

with

$$\sigma_3 = \begin{pmatrix} +1 & 0 \\ 0 & -1 \end{pmatrix} \quad \sigma^+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \sigma^- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

From Zeeman measurements, Eaves *et al.* [9] have shown that the μ_1 and d terms are dominant. A very good fit of the zero field splitting is obtained for the following values (see Fig. 3).

$$\mu_1 = -0.055 \text{ meV} \quad d = -0.07 \text{ meV} \quad \mu_2 = 0.01 \text{ meV} \quad \lambda \sim 0.$$

We have interpreted the spin Hamiltonian parameters and the main conclusions of our calculations (as yet unpublished) are :

- the d and μ_1 terms come from the first order spin-spin interaction and from the second order spin-orbit interaction with the $^5E^*$ excited state,
- the μ_2 term mainly comes from the first order spin-spin interaction while the spin-orbit interaction with the I level, also contributes weakly,
- the spin-spin constant ρ and spin-orbit constant (λ_{T_2}) are weaker than those used by Vallin and Watkins from Cr^{2+} in II-VI compounds [20].

The fact that the spin Hamiltonian does not depend on the strength of the trigonal field (except a weak contribution to the μ_2 term) and that the first order spin-orbit coupling is almost quenched, explains why the overall splitting of the Cr^{2+} and of $\text{Cr}^{2+}\text{-X}$ ground states is the same. This fact has led Voillot *et al.* (see Fig. 2 of [11]) to think that the difference between the two centres was only a weak trigonal field which induced a dynamic Jahn-Teller effect near the static limit.

The transition probabilities can be interpreted by taking $\lambda \sigma_z S_z$ as the Hamiltonian for the 5E excited state. This is the Hamiltonian deduced from Zeeman experiments by Eaves *et al.* [9] and agrees with our model (see Fig. 9 in paper I). In that case, the transition probabilities are accounted for by the μ_1 term alone (the dominant term), and the intensities of the A_1 , A_2 , A_6 and A_7 lines [14] are predicted to be equal. The same is true for the lines B_1 , B_2 , B_6 and B_7 . The A_4 and A_5 lines are forbidden. The polarization of the A_3 and A_4 lines is σ , whereas it is π for the other ones. The electric dipole operators associated with the two polarizations belong to the different representations of C_{3v} . So, the ratio between the intensities of $A_1(A_2, A_6, A_7)$ and A_3 cannot be known *a priori*. Theoretically it should be equal to one half for a weak trigonal field.

As the experimental ratio is close to 1/7, the trigonal field has to be strong. The A_4 and A_5 transitions are weakly allowed by the other terms (d, μ_2) in the spin-Hamiltonian.

4. Intensity of the I and J lines. — In order to describe the splitting between the I and J lines, we have introduced the vibronic coupling (Eq. 2) between the two sets of wavefunctions $E \otimes \varepsilon$ and $A_1 \otimes \varepsilon$. We have also written the vibronic wavefunctions related to the I and J levels by using that type of Hamiltonian (no spin-orbit coupling included). It can be shown that the intensity of the J line (compared to the G line) is only determined by the Jahn-Teller effect in the $^5E^*$ excited state. The weakness of the J line is a proof of the weakness of the Jahn-Teller effect in the excited state. We find that $E_{JT}^* \simeq 1 \text{ cm}^{-1}$. The intensity of the I line is determined both by the Jahn-Teller effect in the excited state and by the coupling Hamiltonian H' . This intensity also depends on the spin-orbit coupling between the I state and the set of ground states. Considering these three effects we get a good value for the I line intensity.

5. Other experiments. — Our model gives explanations of results obtained in other experiments. The complete calculations will be presented elsewhere. The main points can be outlined here : Eaves *et al.* [7, 9] have shown that the field dependence of the Zeeman splitting and its angular dependence could be explained using our model. Uniaxial stress experiments results can also be very well explained. The non-linear behaviour of the splitting for the [100] stress direction comes from the interaction induced by stress between the I level and the doublet ground state. The hydrostatic component obtained by fitting the results is in agreement with that of chromium at a T_d site observed in GaAs under hydrostatic pressure [21].

6. Strength of the trigonal field. — Voillot *et al.* [11-13] used our model, but with the important difference that they supposed the trigonal field weak enough to be quenched in the ground state. However, we believe that all experimental facts cannot be explained if the trigonal field is weak. The most important one is that the ground state is observed to be 5E . This is a result of Zeeman experiments [8-10] due to the number of levels observed in the zero field splitting [14], and also because of the occurrence of the I and J vibronic lines. The reduction of the Jahn-Teller energy between Cr^{2+} and $\text{Cr}^{2+}\text{-X}$ is only consistent with a strong trigonal field. The lowering of the ground state, relative to the band edges ($\sim -100 \text{ meV}$) must also be explained by a non-negligible perturbation acting on the Cr^{2+} centre. The increase of the zero phonon energy ($+19 \text{ meV}$) together with the lowering of the Jahn-Teller coupling also indicates strong perturbation. Skolnick *et al.* [22] proposed that the next neighbour defect X could be an arsenic vacancy ; the other possibility that would explain the fact that the line position is independent of the dominant donor species would be oxygen. In both cases, the trigonal field is expected to be even stronger than our assumption in paper I (900 cm^{-1}). This determination of the trigonal field has not been confirmed by other measurements. Such a value is of course not precise. Moreover the interpretation [4] of the 0.75 eV bump is not the only possible. Anyway, a too low value of the trigonal field (that is to say below 400 cm^{-1}) is not compatible with the experimental results we have just outlined.

7. Conclusions. — We have shown in this paper that the $\text{Cr}^{2+}\text{-X}$ model for the 0.839 eV line in GaAs is adequate to describe all experimental results at zero field.

We have also shown that the trigonal field has to be strong enough, otherwise some features cannot be interpreted such as the occurrence of the I and J lines, and the reduction of the Jahn-Teller effect from isolated Cr^{2+} to $\text{Cr}^{2+}\text{-X}$. Finally, we have given the parameters we obtained for the best fit of the zero field fine structure.

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