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Zeeman spectroscopy of luminescence from vanadium doped gallium arsenide

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Résumé. — Nous présentons les résultats d’expériences de spectroscopie Zeeman sur la luminescence sans phonon à 0,74 eV dans GaAs : V. Nous reconnaissons la transition 3T2 → 3A2 interne à l’ion V3+ (3d2). Une interprétation de ce type avait été avancée par Skolnick et al. pour la luminescence à 0,70 eV de InP : V.

Abstract. — We report the results of Zeeman spectroscopy of the zero-phonon luminescence at 0.74 eV from GaAs : V. They are interpreted in terms of a 3T2 → 3A2 transition within a V3+ (3d2) ion. Such a model was introduced by Skolnick et al. in their study of InP : V.

1. Introduction.

Vanadium in GaP, GaAs, or InP gives rise to a pair of zero-phonon optical lines in luminescence spectroscopy. They are denoted A and B and their energies, in meV, are [1-6] (A = 790.9; B = 792.9), (A = 738.7; B = 740.0) and (A = 705.4; B = 707.0) respectively. A is a cold line and B a hot line. In the GaP crystal, Kaufmann et al. [1] found a doublet structure for the A and B lines.

The Zeeman splitting of the A line in GaP has also been studied by Kaufmann et al. [1]. They interpret the photoluminescence transition as arising from internal levels of the V2+ ion. Skolnick et al. [4] studied the Zeeman splitting of the A line in InP. They assign the optical lines to transitions between internal levels of the V3+ ion.

In this paper we present the Zeeman splitting of the A and B lines in GaAs. The study of the splitting of the B line is important as it is determined primarily by the spin multiplicity of the initial level of the luminescence. We show how our results can be interpreted within the framework of the 3T2 → 3A2 transition in the V3+ (3d2) ion. The difference from the model proposed by Skolnick et al. is in the detailed treatment of the Jahn Teller effect in the 3T2 states. We obtain also an approximate form for the wave-functions for the 3T2 and 3A2 terms which enables us to explain some characteristic features of the optical spectra.

All experiments are carried out in the Voigt configuration, and the bath temperature is 4.2 K.

2. Theory.

2.1 THE MODEL. — The lowest term (3F) of the V3+ (3d2) free ion is split by the cubic crystal field into:

\[ 3A_2 + 3T_2 + 3T_1 \]  

(1)

The splitting scheme is shown in figure 1.

The Jahn Teller coupling with the e-symmetry crystal-modes changes the 3T2 electronic states into 3T2 vibronic states. The degeneracy is lifted by the spin-orbit coupling.

\[ 3T_2 = \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5 \]  

(2)

The magnitudes of the splittings within these four sublevels depend upon the strength of the Jahn Teller coupling. Correct to second order, the projection of the spin-orbit operator into the vibronic 3T2 subspaces is:

\[ \{l \cdot S + \mu (l \cdot S)^2 + \rho (l_x^2 S_x^2 + l_y^2 S_y^2 + l_z^2 S_z^2) \} \]  

(3)

where \( l \) is the effective orbital angular momentum and \( S \) the spin angular momentum; here \( l = 1 \) and \( S = 1 \).

In the strong Jahn Teller coupling limit, the \( \rho \)-term dominates. The main splitting then consists of two sublevels (\( \Gamma_2 + \Gamma_3 \)) and (\( \Gamma_4 + \Gamma_5 \)). The smaller \( \zeta \) and \( \mu \) terms lift the remaining degeneracies as shown in figure 1.
The splitting of the lowest term $^3F$ of the $V^{3+}(3d^2)$ free ion with the crystal-field and spin orbit coupling as perturbations. The vertical lines represent the electric dipole transitions allowed by group theory. The numbers below are proportional to the oscillator strengths calculated in the simplified model (see the text).

The associated wave-functions are deduced from symmetry considerations. For instance the $\Gamma_5(^3T_2)$ zero-order wave functions are:

\begin{align*}
X^* &= \frac{1}{\sqrt{2}}(\xi S_y - \eta S_z) \\
Y^* &= \frac{1}{\sqrt{2}}(\xi S_z - \eta S_x) \\
Z^* &= \frac{1}{\sqrt{2}}(\eta S_x - \xi S_z)
\end{align*}

where $(\xi; \eta; \zeta)$ represents the $T_2$ vibronic basis and $(S_x; S_y; S_z)$ the spin basis.

The spin-orbit interaction transforms the $^3A_2$ level into a $\Gamma_5$ level. The associated zero-order wave-functions are:

\begin{align*}
X &= A_2 S_x \\
Y &= A_2 S_y \\
Z &= A_2 S_z
\end{align*}

where $A_2$ represents the vibronic component.

Spin-orbit interaction will also couple the wave-functions which belong to the different subspaces (namely $^3A_2, ^3T_2, ^3T_1$ in the low-field coupling-scheme theory). For instance if we restrict the coupling to the ground and the first terms only, the spin-orbit interaction mixes the $\Gamma_5(^3A_2)$ and $\Gamma_5(^3T_2)$ wave-functions.

In this approximation, the ground-state wave-functions becomes:

\begin{align*}
X + M X^* \\
Y + M Y^* \\
Z + M Z^*
\end{align*}

where $M$ is the spin-orbit mixing factor. Such a mixing allows $^3T_2 \rightarrow ^3A_2$ electric dipole transitions. The oscillator-strengths are calculated with this simplification in section 4. It will be shown that this provides a satisfying description of the most important features of the spectra. A more sophisticated treatment will be published later. Appendix 1 shows how these oscillator-strengths are calculated.

2.2 THE OPTICAL TRANSITIONS IN THE FREE CRYSTAL. —

A standard table for the reduction of products of representations for the $T_d$ group gives directly the matrix elements for the optical transitions. The predicted transitions and their associated oscillator strengths are given in figure 1. The A and B zero-phonon lines are interpreted as arising from the $\Gamma_5(^3T_2)$ and $(\Gamma_4 + \Gamma_5)(^3T_2)$ sublevels respectively. This give the following values (in meV) for $\rho = -2.0$ for GaP, $-1.25$ for GaAs and $-1.55$ for InP.

The predicted fine structure of the B line shown in the figure 1 was resolved by Kaufmann et al. (1982) in GaP. Such a result cannot be explained in terms of a pure static Jahn Teller model. In GaP, the authors also observed a small shoulder at the high energy end of the A line. We suggest that this small structure is the effect of internal strain.

2.3 THE ZEEMAN SPLITTINGS. —

The direct projection of the Zeeman operator onto the vibronic $^3T_2$ subspaces is:

\begin{align*}
\mu_B(\gamma I + gS).H
\end{align*}

Fig. 2. — The theoretical splitting of the initial ($^3T_2$) and final ($^3A_2$) states as a function of the magnetic field. The numbers specify the irreducible representation (1 for $\Gamma_1$, 2 for $\Gamma_2$, ...) and $S_4$, $C_2$, $C_3$ are the symmetry point group when $H//\{001\}, \{110\}$ and $\{111\}$ respectively.
where $\gamma$ includes the Jahn-Teller reduction and cova-
lency effects. We take $g = 2$ and $\gamma = 0$ so that the
Zeeman operator has exactly the same projection in
the excited ($^{3}T_{2}$) and ground ($^{3}A_{2}$) subspaces. The
theoretical splittings which are anisotropic and iso-
tropic respectively are calculated by matrix dia-
gonalization and drawn in figure 2. This diagonalization
gives also the associated states, the symmetries of
which are indicated in the figure. The oscillator-
strengths of the electric dipole transitions can then
be calculated.

3. The experiment.

$\mathbf{H}/[110]$.

The splittings in a magnetic field of up to 7 T are
shown in figure 3. The experimental points (dots in the
figure) were obtained from successive spectra like
those shown in figure 4. The experimental conditions
for recording the A and B spectra are different. The
laser power is higher and the spectroscopic resolution
lower for B. The curves show the complete theoretical
splittings. All the electric dipole transitions are allowed
by group-theory but some of them (broken lines)
are zero in the simplified model discussed in section 4.

As in the case of InP : V [4], the A line splits into
three almost equally-spaced and well separated dou-
blets labelled $(A_1, A_1'), (A_2, A_2'), (A_3, A_3')$. The therma-
lization effects observed in InP : V by Skolnick et al.[4]
have been verified here. $A_1'$, $A_2'$, $A_3'$ are cold lines
and $A_1$, $A_2$, $A_3$ are hot lines. This proves that the
doublet splitting occurs in the initial state of the
transitions

$\mathbf{H}/[001]$.

The splitting in a magnetic field of up to 7 T is
shown in figure 5. The experimental points (dots) were
obtained from successive spectra like those reported
in figure 6. Again the experimental conditions for
recording the A and B spectra are different (see above).
The curves give the theoretical splitting. Only the
electric dipole transitions allowed by group theory
have been reported, the broken lines being associated
with transitions forbidden only in the simplified
model discussed in section 4.

We have verified that $A_1$ and $A_3$ are hot lines while
$A_1'$, $A_2'$, $A_3'$ are cold lines.

The B line splits into three almost equally spaced,
well separated doublets. The splitting pattern of the B
line is nearly a mirror-image of the splitting pattern
of the A line at high energy.

$\mathbf{H}/[111]$.

The splitting in a magnetic field of up to 7 T is
shown in figure 7. The experimental points (dots) were
obtained from successive spectra like those reported
in figure 8. The full curves represent the
theoretical splitting. For this direction of $\mathbf{H}$, all the
Fig. 5. — $\mathbf{H}/[001]$. Fan chart of the spectra of figure 6 for the 740.0 and 738.7 meV ZPL up to magnetic fields of 7 T. The dots are experimental points. The curves are theoretical; only the electric dipole transitions allowed by group-theory have been considered — the broken lines indicate the transitions which are zero in the simplified model (see the text).

Fig. 6. — $\mathbf{H}/[001]$. The 740.0 and 738.7 meV ZPL for GaAs : V in liquid helium with magnetic field increasing from top to bottom. The magnetic field intensity, in units of tesla, is indicated on the right of the spectra.

Fig. 7. — $\mathbf{H}/[111]$. Fan chart of the spectra of figure 8 for the 740.0 and 738.7 meV ZPL for magnetic fields of up to 7 T. The dots are experimental points. The curves are theoretical. In this direction all the transitions are allowed by group theory and by the simplified model (see the text).

Fig. 8. — $\mathbf{H}/[111]$. The 740.0 and 738.7 meV ZPL for GaAs : V for magnetic field increasing from top to bottom. The magnetic field intensity, in units of tesla, is indicated on the right of the spectra.
transitions are allowed by group-theory and by the simplified model discussed in section 4.

3.1 THE ZEEMAN ANISOTROPY. — The Zeeman anisotropy of the A line at 6 T for a magnetic field rotated in the [110] crystallographic plane is presented in figure 9. The dots represent the experimental points and the full curves are theoretical without adjustment, taking \( g = 2 \) for both the ground and excited states.

![Fig. 9. — The Zeeman anisotropy in GaAs : V of the 738.7 meV ZPL at 6 T for magnetic fields in the [110] crystallographic plane. The dots are experimental points and the full curves are theoretical.](image)

4. Theoretical spectra.

In figure 10 we present theoretical Zeeman spectra in the A line region (739-738 meV). The positions of the lines are obtained from the Hamiltonians (3) and (7) for the excited states (\( \rho = -1.25 \text{ meV}, \ g = 2 \) and \( \zeta = \mu = \gamma = 0 \)) and from the Hamiltonian (7) for the ground states \( (g = 2, \ \gamma = 0) \). The lineshapes are taken as Lorentzian of equal width. The intensities are calculated via the simplified framework given in section 2. A Boltzmann factor has been included and the sample temperature assumed is 4.2 K.

The best agreement between experimental and theoretical spectra (i.e. between the Figs. 6 and 9a, and 9b and 8 and 9c respectively) are for the [111] and [001] directions of the magnetic field. It is excellent for the [111] direction, while slight discrepancies can be noticed between the relative intensity of the cold \((A_1', A_2', A_3)\) and hot \((A_1, A_3)\) lines in the [001] direction.

For the [110] direction, the simplified theory does not predict the \( A_2' \) line though the transition is allowed according to the group-theory.

This means that the consideration of spin-orbit mixing between the \( ^3T_2 \) and \( ^3A_2 \) states only is able to give many of the important features of the experimental spectra but not their full interpretation.

5. Conclusion.

The luminescence spectroscopy at 0.74 eV from GaAs : V in the presence of a magnetic field confirms the previous suggestion of Skolnick et al. that it arises from the \( ^3T_2 \rightarrow ^3A_2 \) transition within a \( V^{3+}(3d^2) \) ion. The \( T_2 \) electronic states are strongly coupled to the \( e \) crystal-modes, but the Jahn Teller effect is dynamic and not static. A simplified spin-orbit interaction scheme gives us a crude description of the optical intensities. We believe that the model is the same for both GaP : V and InP : V in which the zero-phonon optical transitions occur at 0.79 and 0.70 eV respectively.

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Post data.

Luminescence spectroscopy under uniaxial stress has been performed recently in our laboratory. The results confirm entirely the present interpretation of the defect. They are published separately in J. Phys. C : Solid State Phys.
Appendix 1.

In this Appendix we show how the oscillator-strengths are calculated.

The probability of an optical transition occurring between \( |i\rangle \) and \( |j\rangle \) is proportional to:

\[
|\langle i | H_{\text{optical}} | j \rangle|^2
\]

where

\[
H_{\text{optical}} = \sum_x \vec{e} \cdot \vec{r}_x.
\]

For the dipolar-electric transition \( \vec{e} \) is the unit vector along the electric field of the light and \( \vec{r}_x \) is the position vector of the \( x \)-th electron relative to the nucleus of the ion.

The orbital components of the zero-order wave functions of the \( \Gamma_x(3T_2), \Gamma_y(3T_2), \Gamma_z(3T_2) \) and \( \Gamma_x(3T_2) \) states are \( (z, \eta, \zeta) \) and belong to the same representation \( T_2 \) (for example, the \( \Gamma_z(3T_2) \) zero-order wave functions are given in (4)). According to our restricted coupling the active part of the orbital components of the ground state wave functions \( \Gamma_x(3A_2) \) are also \( (z, \eta, \zeta) \) (see (6)). In this scheme and restricting ourselves to the dipolar electric transitions we can set up table I, which gives the matrix elements between the excited and ground states.

In this table \( \{ U^*, V^*, W^* \} \) and \( \{ \theta^*, e^* \} \) represent the \( \Gamma_x(3T_2) \) and \( \Gamma_z(3T_2) \) zero-order wave functions respectively. The polarization is specified by the symbol between brackets and \( A = \langle T_2/\vec{e}, \vec{r}/T_2 \rangle \).

To calculate the spectra shown in figure 10 we need to know which is the associated state for each energy level.

A matrix diagonalization of the operator \( H_{\text{so}} + H_{\text{Zeeman}} \{ (3) + (7) \} \) is performed in the excited state \( 3T_2 \), and a matrix diagonalization of \( H_{\text{Zeeman}}(7) \) is performed in the ground state \( 3A_2 \). This gives us the energy levels and their associated eigenstates which are linear combinations of the \( 3T_2 \) and the \( 3A_2 \) wave functions respectively. For example, when the magnetic field is applied along the [001] direction, the \( \Gamma_x(3A_2) \) state for the ground level is \( (Z + MZ^*) \).

Then, using table I we can calculate the theoretical spectra of figure 10.

Table I.

<table>
<thead>
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<th>( X + MX^* )</th>
<th>( \theta^* )</th>
<th>( e^* )</th>
<th>( X^* )</th>
<th>( Y^* )</th>
<th>( Z^* )</th>
<th>( U^* )</th>
<th>( V^* )</th>
<th>( W^* )</th>
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<td>( -A )</td>
<td>0</td>
<td>( -A )</td>
<td>( A )</td>
</tr>
<tr>
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<td>( -A )</td>
<td>( A )</td>
<td>0</td>
<td>( -A )</td>
</tr>
<tr>
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<td>( -A )</td>
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<td>( -A )</td>
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