Proceedings of the Third International Workshop on Materials Science (IWOMS '99), Hanoi, November 2-4, 1999

Spectroscopy of rare-earth doped semiconductors: energy levels of ytterbium in indium phosphide

C.A.J. Ammerlaan and I. de Maat-Gersdorf
Van der Waals-Zeeman Institute, Faculty of Mathematics, Computer Science, Physics and Astronomy, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

In its regular charge state Yb^{3+}, the ytterbium impurity in indium phosphide has the electronic configuration $4f^{13}$, orbital momentum L = 3 and spin S = 1/2. Ground and excited states with the total spins J = 7/2 and J = 5/2, respectively, are formed by spin-orbit interaction. The EPR spectrum of the center provides by resolved hyperfine interactions with the isotopes ^{171}Yb (nuclear spin I = 1/2, natural abundance α = 14%) and ^{173}Yb (I = 5/2, α = 16%) direct evidence for a one-ytterbium center in high-symmetry environment. The optical transition between the excited and ground states with an energy around 10020 cm^{-1} (λ = 0.998 μm) is easily observed in photoluminescence. A cubic crystal field lifts the eight-fold degeneracy of the ground state into a Γ_6 doublet, a Γ_7 doublet and a Γ_8 quartet; also the excited state is split by the crystal field. The ordering of the crystal field levels is still a matter of discussion, both for the ground and excited spin-orbit multiplets. Several experiments providing information on the ordering will be briefly discussed. These include the luminescence intensity, temperature, stress and magnetic field dependence in fields up to 16 Tesla, magnetic resonance, together with a crystal field analysis. A conclusion towards a Γ_7 - Γ_6 - Γ_8 ordering for the ground state multiplet and Γ_7 - Γ_8 for the excited state multiplet, known as the Masterov model, will be drawn.

1. Introduction

Among rare-earth impurities in semiconductors the system of ytterbium in indium phosphide has been frequently investigated. The optical and magnetic properties are to first order determined by the atomic states of the 4f inner shell electrons. In a Russell-Saunders scheme the orbital and spin momenta of individual electrons couple separately to total L and S. By spin-orbit interaction multiplets characterized by total momentum J are formed. The crystal field of the semiconductor environment lifts the degeneracies of the spin-orbit levels. Due to shielding by outer 5s and 5p electrons these splittings are relatively small and can be treated as a perturbation on the atomic level diagram. As regards the ordering of the levels of InP:Yb some different schemes have been derived [1,2]. In this paper experimental results providing relevant information on the crystal field effect will be discussed.

2. Energy levels

2.1 Spin-orbit interaction

In the case of ytterbium in indium phosphide, in the regular charge state Yb^{3+} with electron configuration $4f^{13}5s^25p^6$, the one hole in the otherwise full 4f shell leads to orbital momentum L = 3 and spin S = 1/2. By spin-orbit coupling $\mathcal{H}_{so} = \lambda \mathbf{L}.\mathbf{S}$ the multiplets $^2F_{5/2}$ with J = 5/2 and $^2F_{7/2}$ with J = 7/2 are formed. Ground and excited states are separated by (7/2)λ, experimentally determined as 10020 cm^{-1}. As $\lambda < 0$, the eight-fold degenerate $^2F_{7/2}$ multiplet forms the ground state. Figure 1 illustrates the spin-orbit level diagram.

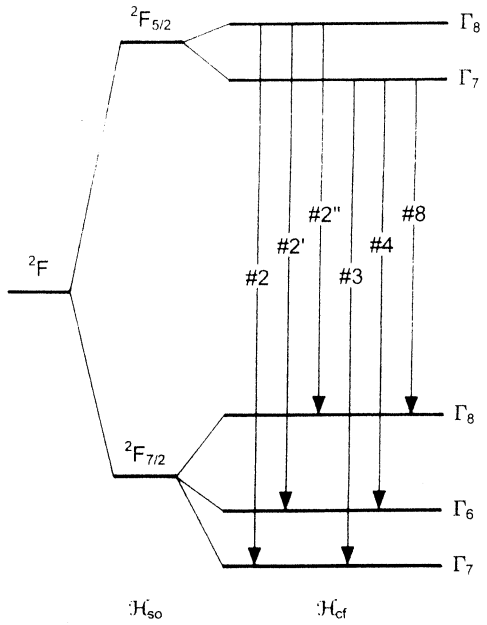

Fig. 1: Energy level diagram of InP:Yb^{3+} illustrating spin-orbit (so) and crystal-field (cf) splittings, with level assignment following Masterov, *et al.* [1]. The labeling of zero-phonon transitions is also indicated.

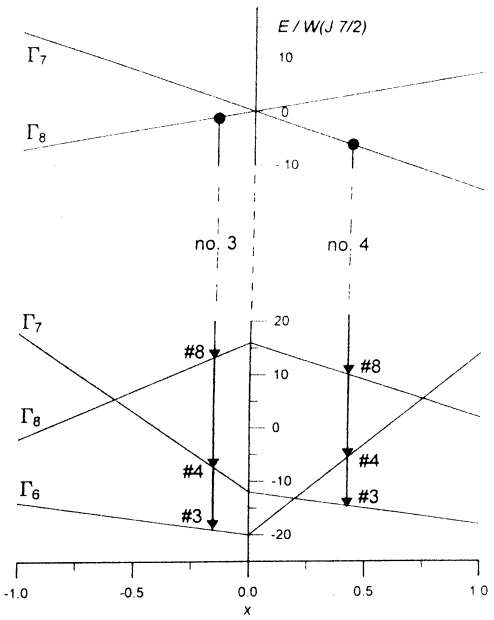

Fig. 2: Diagram of crystal-field energy levels E/W as a function of x, in the range $-1 \leq x \leq +1$, for $W > 0$ for both excited state $^2F_{5/2}$ and ground state $^2F_{7/2}$, following Lea, *et al.* [3]. The solution of models no. 3 and no. 4 is indicated.

2.2 Crystal-field interaction

When embedded in a host crystal the atomic states of the rare-earth impurity will be affected by the crystal field. As following from group theoretical considerations the ground state $^2F_{7/2}$ will be split into three levels of doublet Γ_6, doublet Γ_7 and quartet Γ_8 character; the excited state will separate into a Γ_7 doublet and a Γ_8 quartet. For a quantitative description the suitable general crystal-field Hamiltonian, applicable to a center of cubic symmetry with spin $J \leq 7/2$, is

$$\mathcal{H}_{cf} = (b_4/60)O_4 + (b_6/1260)O_6. \quad (1)$$

In an equivalent alternative form the Hamiltonian has been given with parameters W and x [3] related to b_4 and b_6 by $b_4 = Wx$ and $b_6 = W(1 - |x|)$, with $-1 \leq x \leq +1$. Operators O_4 and O_6 represent the 4th- and 6th-order angular momentum operators, respectively. On application of operator $\mathcal{H}_{cf}$ the crystal field levels are obtained as

$$E(^2F_{7/2},\Gamma_6) = +(3/2)\lambda + 14b_4 - 20b_6, \quad (2)$$

$$E(^2F_{7/2},\Gamma_7) = +(3/2)\lambda - 18b_4 - 12b_6, \quad (3)$$

$$E(^2F_{7/2},\Gamma_8) = +(3/2)\lambda + 2b_4 + 16b_6, \quad (4)$$

$$E(^2F_{5/2},\Gamma_7) = -2\lambda - (44/3)b_4, \quad (5)$$

and

$$E(^2F_{5/2},\Gamma_8) = -2\lambda + (22/3)b_4. \quad (6)$$

The level diagram for the case $W = +1$ as a function of x, covering the full range $-1 \leq x \leq +1$, is illustrated by figure 2.

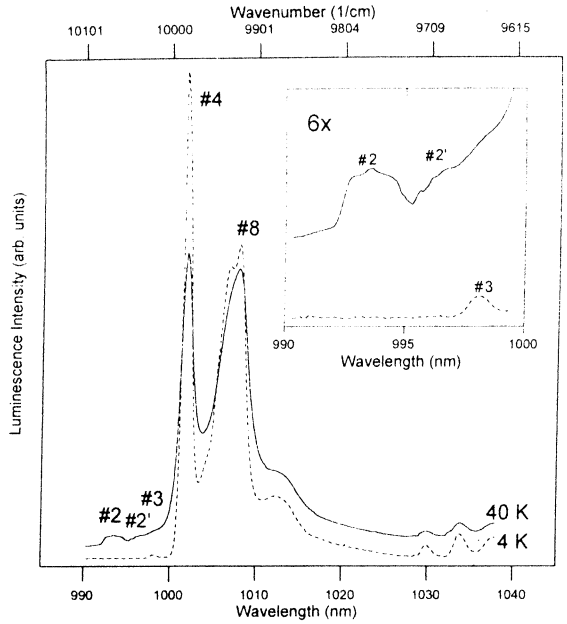

Fig. 3: Photoluminescence spectrum of InP:Yb measured at temperature T = 4 K (dashed curve) and at T = 40 K (solid curve). The zero-phonon transitions are labeled #2, #2', #3, #4 and #8. The insert shows the hot lines #2 and #2' and line #3 six times amplified.

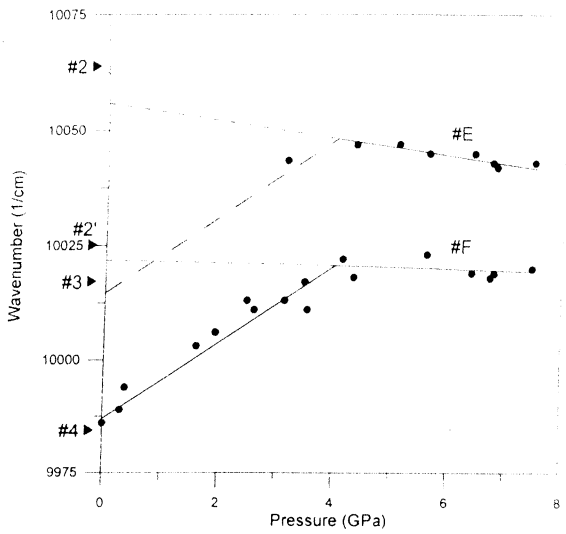

Fig. 4: Positions of the luminescence lines as a function of hydrostatic pressure, after Stapor, *et al.* [4]. Dashed lines are extrapolations of the high-pressure emissions #E and #F to zero pressure. Positions of lines #2, #2', #3 and #4 at zero stress are indicated along ordinate axis.

2.3 Transition energies

Transitions between these levels are observable in a luminescence experiment; a photoluminescence spectrum is given in figure 3. At liquid-helium temperature only the lowest crystal-field level of excited state $^2F_{5/2}$ is populated and a total of three transitions is available. In the experimental spectrum these are identified with the zero-phonon transitions labeled #3, #4 and #8 at the energies E(#3) = 10018 cm^{-1}, E(#4) = 9982.5 cm^{-1} and E(#8) = 9922.5 cm^{-1}. From these observed energies the parameters λ, b_4 and b_6 (alternatively λ, W and x) can be calculated. The six possible solutions, corresponding to different ordering of levels in the $^2F_{7/2}$ ground state, are given in table 1. It remains to be decided which of these models fits best to available experimental and theoretical data. In the next section this will be discussed.

3. Energy level ordering

3.1 Photoluminescence intensity

On comparing intensities of zero-phonon emissions it is apparent that the intensity of the luminescence line labeled #3 is much smaller than those of #4 and #8. For transitions which are electron-dipole induced the probability is given by a matrixelement $\langle\Gamma_i|\mathbf{E}_{dip}|\Gamma_f\rangle$. The initial state Γ_i, to be taken from the $^2F_{5/2}$ multiplet, has symmetry type Γ_7 or Γ_8. The final state, in the ground state $^2F_{7/2}$, is from representations Γ_6, Γ_7 or Γ_8. Among all possibilities matrixelement $\langle\Gamma_7|\mathbf{E}_{dip}|\Gamma_7\rangle$ is vanishing for symmetry reasons, all others have a finite value. On this basis the luminescence line #3 is assigned to a Γ_7 to Γ_7 transition. This, as can be verified in table 1, holds for models 1 and 4.

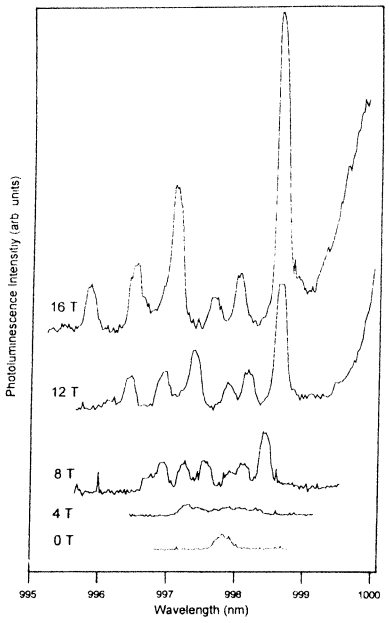

Fig. 5: Transition #3 of the luminescence spectrum of InP:Yb^{3+} in several magnetic fields up to 16 T.

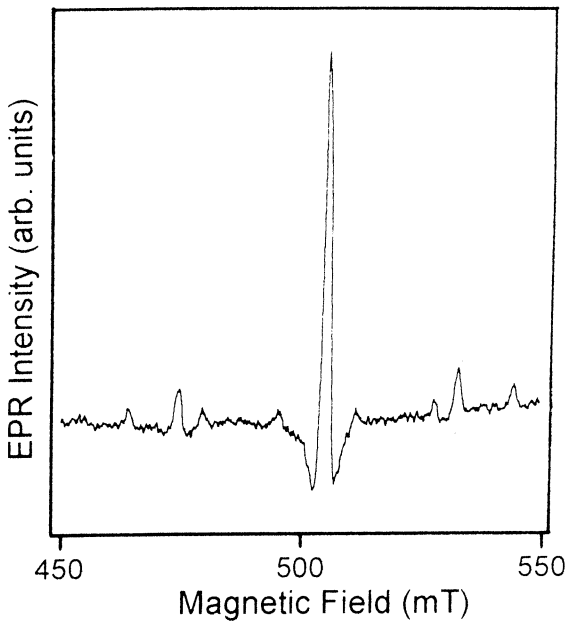

Fig. 6: Electron paramagnetic resonance (EPR) spectrum of Yb^{3+} in InP recorded at the microwave frequency $\nu \approx 23$ GHz, temperature T = 4 K.

3.2 Photoluminescence temperature dependence

At higher temperatures the upper crystal-field level of the excited state $^2F_{5/2}$ will become populated. This will lead to additional lines in the emission spectrum, so-called hot lines, labeled 2, 2' and 2" in the diagram of figure 1. In the actual luminescence the weak lines 2 and 2' at wavenumbers 10064 and 10025 cm^{-1}, respectively, appear upon increasing the temperature from 4 to 40 K, as can be seen in figure 3. From these observations the crystal-field splitting of the $^2F_{5/2}$ multiplet is calculated as E(#2) – E(#3) = +46 cm^{-1} or E(#2') – E(#4) = +43 cm^{-1}. In the crystal-field analysis this splitting is given by $E(^2F_{5/2},\Gamma_8) - E(^2F_{5/2},\Gamma_7) = 22b_4$. The result $b_4 \approx \pm 2.0$ cm^{-1} matches best with models 4 and 5. Observation of the hot line #2' is reported here for the first time. Transition 2" is hidden under the strong emission #4 and remains invisible.

3.3 Photoluminescence hydrostatic-stress dependence

Under hydrostatic pressure the luminescence transitions were observed to change their energies linearly [4]. E.g., the transition #4 increases in energy by +7.80 cm^{-1}/GPa. However, at pressures of 4.1 GPa and above line #4 is no longer present. It appears to be replaced by a different line, labeled #F, with a different amplitude and width, and a pressure dependence of –0.32 cm^{-1}/GPa. Extrapolating line #F to zero pressure, as shown in figure 4, the intersection happens close to the energy of line #2'. This suggests that line #2', the hot line at pressures below 4.1 GPa, becomes the "cold" line above 4.1GPa. The role of line #4 is opposite. A similar effect occurs for transition #3 at pressure below 4.1 GPa, transition #E at high pressure with an extrapolation to hot line 2 at zero stress. The two crystal-field levels of the $^2F_{5/2}$ state cross at stress 4.1 GPa and move towards each other by 8.12 cm^{-1}/GPa. They are therefore separated at zero stress by 33.3 cm^{-1}. Equating the splitting to the crystal-field expression $22b_4$, one obtains $b_4 = 1.51$ cm^{-1}. This result is in best agreement with models 2 and 4, as marked in table 1.

Table 1: Summary of the analysis relevant to the ordering of crystal-field levels in the ground state $^2F_{7/2}$ and excited state $^2F_{5/2}$ of Yb^{3+} in InP. For each of the six models considered the crystal-field parameters of Hamiltonian equation (1), either b_4 and b_6 or W and x, are given. In the lowest five rows of cells best agreement with experiments or theory is indicated by the + symbol.

Model no.		1	2	3	4	5	6
b_4 (cm^{-1})		+2.85	+1.37	–0.47	+1.68	–2.38	–2.98
b_6 (cm^{-1})		–0.77	–2.25	+2.55	+2.28	+1.78	–0.01
x		–0.78	–0.38	–0.15	+0.42	+0.57	+1.00
W (cm^{-1})		–3.62	–3.62	+3.02	+3.96	–4.16	–2.98
$^2F_{5/2}$		Γ_8	Γ_8	Γ_7	Γ_8	Γ_7	Γ_7
		Γ_7	Γ_7	Γ_8	Γ_7	Γ_8	Γ_8
$^2F_{7/2}$		Γ_6	Γ_6	Γ_8	Γ_8	Γ_7	Γ_7
		Γ_8	Γ_7	Γ_7	Γ_6	Γ_6	Γ_8
		Γ_7	Γ_8	Γ_6	Γ_7	Γ_8	Γ_6
Intensity #3		+			+		
Hot lines #2 and #2'					+	+	
Stress effect			+		+		
Magnetic resonance		+			+		
Co-ordination	4 fold				+		
	6 fold			+			

3.4 Photoluminescence magnetic-field dependence

In a magnetic field all degeneracy of the levels is lifted. In the luminescence spectrum the lines will split into components as dictated by the number of magnetic substates in both initial and final states of the transition. Figure 5 shows such a result for emission #3 in magnetic fields up to 16 T. From the number of components, in agreement with data as also given in [2], the transition #3 is readily interpreted as being between a doublet Γ_6 or Γ_7 state and a Γ_8 quartet state. This appears to be a most valuable result. In the specific case of InP:Yb care must be exercised, however. It has been observed that while performing the experiment, having the sample subjected to high-intensity laser radiation while being in a high magnetic field, the luminescence spectrum changed dramatically, with spectral lines disappearing and new lines at different positions growing in. This is described as the transformation of the Yb center from an original standard state I to a new state II, which shows a permanent character. It requires annealing at temperatures above 200 K to re-establish state I. The phenomenon is not understood in electronic or atomic microscopic terms. From experimental conditions it is concluded that observed magnetic splittings are for the new state II. For this reason the experimental findings on Zeeman splittings are not used in the level assignments. The unusual phenomenon requires further study.

3.5 Magnetic resonance

The electron paramagnetic resonance (EPR) spectrum of the InP:Yb center, shown in figure 6, has been frequently observed. By the resolved characteristic hyperfine interactions for the isotopes ^{171}Yb, with nuclear spin I = 1/2 and natural abundance α = 14%, and the isotope ^{173}Yb, I = 5/2 and α = 16%, the center is unambiguously identified as a one-ytterbium center. The spectrum is isotropic indicating an undistorted substitutional or

a tetrahedral interstitial position for the ytterbium ion. The experimental Zeeman splitting factor is g = 3.291. From a theoretical treatment of their magnetic properties, the crystal field states in the $^2F_{7/2}$ multiplet are characterized by electron spin S = 3/2 and anisotropic g tensor for the Γ_8 quartet, spin S = 1/2 with isotropic g value g = 8/3 for the Γ_6 doublet and spin S = 1/2 with isotropic g value g = 24/7 for the Γ_7 doublet. This provides solid evidence for the identification of the ground state as the Γ_7 doublet, as offered in models 1 and 4. The reduction of the experimental g value by a few percents compared to the theoretical value is evidence for some delocalization of the 4f electrons of Yb in the InP crystal.

3.6 Coordination

The crystal field as experienced by the ytterbium ion depends on its surrounding by ions of the InP crystal. In case the ytterbium ion occupies a substitutional site the crystal field is determined by interaction with the four nearest-neighbor phosphorus atoms, in a tetrahedral configuration. In a point-charge model the 4th-order potential will be represented in Eq. (1) by the parameter $B_4 = b_4/60 = -(7/36)(Ze^2/R^5)\langle r^4\rangle\beta$, the coefficient for O_6 will be given by $B_6 = b_6/1260 = +(1/18)(Ze^2/R^7)\langle r^6\rangle\gamma$ [3]. Although a point-charge approximation may not always give exact quantitative results, it is generally observed to yield the correct signs of parameters. The constants β and γ are the Stevens multiplicative factors with the values $\beta = -0.00173$ and $\gamma = +0.00015$ for the $4f^{13}$ configuration of Yb^{3+} in the $^2F_{7/2}$ state. The argument shows that both b_4 and b_6 are positive, from where it follows that also $x > 0$ and $W > 0$. This complies with level model no. 4. In a similar manner one derives for an interstitial site of Yb^{3+}, with a six-fold octahedral coordination, $b_4 < 0$ and $b_6 > 0$, and correspondingly $x < 0$, $W > 0$. This is the situation for model no. 3. Conclusions are represented in table 1.

4. Conclusions

In the presented analysis the splitting of spin-orbit levels of Yb^{3+} in InP has been considered assuming validity of a crystal-field description. Evidence from several experiments, such as the effects of temperature, magnetic field and hydrostatic pressure on the photoluminescence spectrum, have given the most probable crystal field parameters. For the preferred model, number 4 as apparent by an inspection of table 1, these are W = +3.96 cm^{-1} and x = +0.42. The level ordering is $\Gamma_7 - \Gamma_6 - \Gamma_8$, from low to high energies, for the $^2F_{7/2}$ spin-orbit ground state multiplet and $\Gamma_7 - \Gamma_8$ for the $^2F_{5/2}$ excited state multiplet. This result confirms the earlier assignment of Masterov, *et al.* [1]. Crystal-field parameters are consistent with an undistorted substitutional site for the Er ion on the indium sublattice. In the course of the experiments a new hot line, labeled #2', was observed at a measuring temperature of 40 K. New lines appearing in the luminescence spectrum under hydrostatic stress above 4 GPa were interpreted as arising from a crossing of the two sublevels in the $^2F_{5/2}$ state.

References

[1] V.F. Masterov, V.V. Romanov and K.F. Shtel'makh, Sov. Phys. Solid State **25** (1983) 824.

[2] G. Aszodi, J. Weber, Ch. Uihlein, L. Pu-lin, H. Ennen, U. Kaufmann, J. Schneider and J. Windscheif, Phys. Rev. B **31** (1985) 7767.

[3] K.R. Lea, M.J.M. Leask and W.P. Wolf, J. Phys. Chem. Solids **23** (1962) 1381.

[4] A. Stapor, A. Kozanecki, K. Reimann, K. Syassen, J. Weber, M. Moser and F. Scholz, Acta Phys. Pol. **79** (1991) 315.