THE 4f INTRASHELL TRANSITIONS OF YTTERBIUM IN INDIUM PHOSPHIDE

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ABSTRACT

Zeeman measurements in magnetic fields up to 16 T have been performed on the no-phonon lines labelled #3, #4, and #8 of the spectrum of ytterbium impurities in indium phosphide. A strong polarization effect and changes in intensities were observed. An energy level diagram is presented that satisfactorily explains the magnetic field effect and the relative intensities of the photoluminescence lines and is consistent with experiments described in the literature.

INTRODUCTION

Rare-earth doped semiconductors are lately intensively investigated in the prospective of their possible application in optoelectronic devices. The presence of an incompletely filled 4f shell offers an attractive possibility of inducing intrashell excitations, with a sharp atomic-like spectrum, practically independent of the host crystal.

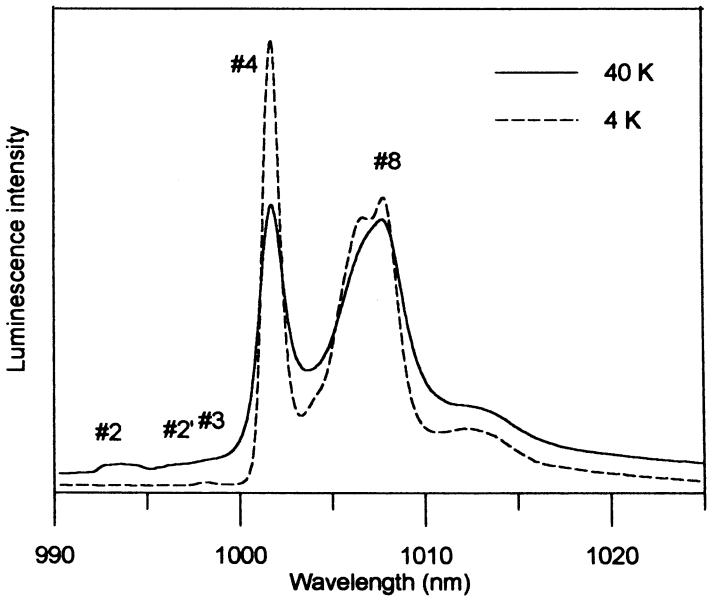

Figure 1. The photoluminescence spectrum of InP:Yb at 4 and 40 K with the observed transitions indicated [7].

Ytterbium in indium phosphide is one of the best investigated systems [1-5]. Ytterbium in its trivalent state, Yb^{3+} ($4f^{13}$), most probably placed substitutionally on a cation site in the InP lattice, always shows a characteristic luminescence spectrum at a temperature of 4K, see figure 1. The lines #2, #3, #4, and #8, at 10064, 10018, 9982.5, and 9922.5 cm^{-1}, or 994, 998, 1001, and 1008 nm, respectively, are interpreted as no-phonon transitions. The origin of the other lines is not completely established; they are

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described as phonon replica's [3] or assigned to a non-cubic centre [4]. The zero-phonon lines are shown to result from a cubic defect centre and arise from transitions between the spin-orbit levels $^2F_{5/2}$ and $^2F_{7/2}$. Due to the cubic crystal field the lower $^2F_{7/2}$ level is split in three, Γ_6, Γ_7, and Γ_8 sublevels, and the $^2F_{5/2}$ in two, a Γ_7 and a Γ_8 sublevel.

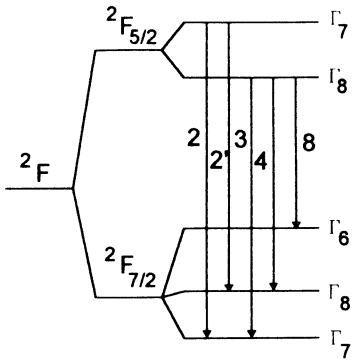

Figure 2. The energy level diagram of InP:Yb according to Ref. [3].

Zeeman measurements [3] show an eightfold splitting of line #3 in high magnetic fields. Following this study an energy level diagram for the 4f sublevels, as shown in figure 2, has been established. This scheme has an unusual reversal of the Γ_7 and Γ_8 sublevels at the excited state that cannot be explained by the crystal field calculations [6], and is in contrast to the predictions of a point charge model for an ytterbium atom on a substitutional cation site [8]. Further, in this scheme one is unable to explain the relative intensities of the lines #3, #4 and #8 in photoluminescence and the surprising increase of the luminescence intensity of line #3 when applying a magnetic field, see later.

Optically detected magnetic resonance (ODMR) has been observed in the lowest state of the $^2F_{5/2}$ level [4]. The ODMR signal is not isotropic but depends on the crystal orientation relative to the magnetic field; this can be interpreted as a confirmation of the reversed order of the crystal field states in the $^2F_{5/2}$ level.

EXPERIMENTAL RESULTS AND DISCUSSION

Lines #3, #4 and #8 in the luminescence spectrum of Yb in InP have been studied by investigating their Zeeman effect at a temperature of 4 K in magnetic fields up to 16 tesla. The luminescence was excited with a cw argon-ion laser operating at a wavelength of 514.5 nm. A 0.64 m monochromator, with an unblazed 1200 grooves mm^{-1} grating, was used in a backscattering geometry with $\lambda/4$ and polarization filters. The light emerging parallel to the field direction was observed. The magnetic field was changed 180 degrees to measure the different polarizations; in this paper an arbitrarily chosen direction will be referred to as positive.

Two samples were used in this study:
- One crystal was grown by metal-organic chemical vapour deposition (MOCVD). The total Yb concentration was approx. 10^{18} atoms/cm^3. The surface was the [100] plain.
- The other crystal was grown by the high pressure gradient freeze synthesis method. By this method, Yb was diluted in indium phosphide with a concentration of about 10^{17} atoms/cm^3. The surface of this sample was off-axis oriented.

When investigating the transitions that are possible in this system selection rules should be taken into account. For the magnetic field split levels these are $\Delta\mu = 0$ or $+/- 1$, with μ the lowest (absolute) value of the magnetic quantum number *m*. For electrical dipole-transitions $\Delta\mu = 0$, linear polarized light will be emitted perpendicular to the magnetic field. In the case of $\Delta\mu = +/-1$ transitions circular polarized light will be emitted parallel or antiparallel to the magnetic field. Since the experiment was done in the latter configuration the selection rules are $\Delta\mu = +/-1$.

We will first investigate what to expect for the different transitions of Yb in a <100> direction. The forbidden $\Gamma_7 \rightarrow \Gamma_7$ transition has four possible components: one with $\Delta\mu = +1$, one with $\Delta\mu = -1$ and two with $\Delta\mu = 0$; the allowed transitions are the inner ones. According to this scheme the $\Gamma_7 \rightarrow \Gamma_7$ transition is permitted; probably in T_d symmetry the different contributions of this line will sum up to zero because of destructive interference. Without field there is no line but as soon as the Zeeman splitting is bigger than the natural line width two strong lines will be seen.
The $\Gamma_7 \rightarrow \Gamma_6$ transition has also two allowed components $\Delta\mu = +/-1$ but they are the outer ones and the other two have $\Delta\mu = 2$. The $\Gamma_7 \rightarrow \Gamma_8$ transition and the $\Gamma_8 \rightarrow \Gamma_7$ transition will both have in total eight components two $\Delta\mu = 0$, two $\Delta\mu = 2$ and four allowed transitions; the allowed ones are the inner ones. The $\Gamma_8 \rightarrow \Gamma_6$ transition is similar, with the allowed lines being the outer ones. Finally, for $\Gamma_8 \rightarrow \Gamma_8$ there are four $\Delta\mu = 2$, four $\Delta\mu = 0$ and eight allowed transitions, the inner ones.
When the field is in an arbitrary direction, no transitions will be forbidden. In this case a doubling of the number of lines is expected when compared to the situation for the <100> direction. In what follows the results obtained for the individual spectral components will be discussed.

Line #8

In the Zeeman splitting of line #8 at 1007.7 nm, two lines were resolved for the <100> direction, and four for the off-axis direction, see figures 3 and 4. The total splitting width is about 4 nm in a field of 16 T. More components observed in this region are most probably due to the lines #5 - #7. The intensity of the four lines changed with increasing field. The intensity of the lines seen in the positive polarization got somewhat higher and the intensity of the lines seen in negative direction decreased, see figure 5.
In theory the Zeeman components are expected to repel each other, see figure 6. In the experiment a deviation from the expected behaviour is seen indicating that a rather strong second-order effect is present. One can assume that also lines #3 and #4 are influenced by this effect and this will disturb correct qualitative analysis of the Zeeman effect.
The very clear splitting of line #8 into two components for the <100> oriented sample and four in the low-symmetry direction indicates that this line must correspond to a $\Gamma_7 \rightarrow \Gamma_7$ or a $\Gamma_7 \rightarrow \Gamma_6$ transition. Also the fact

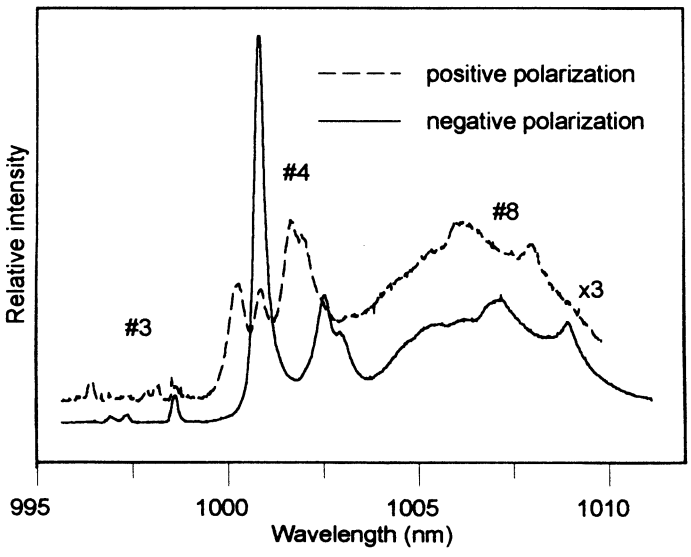

Figure 3. The Zeeman spectra observed in the positive and negative polarization at 14 T, in the off-axis oriented sample.

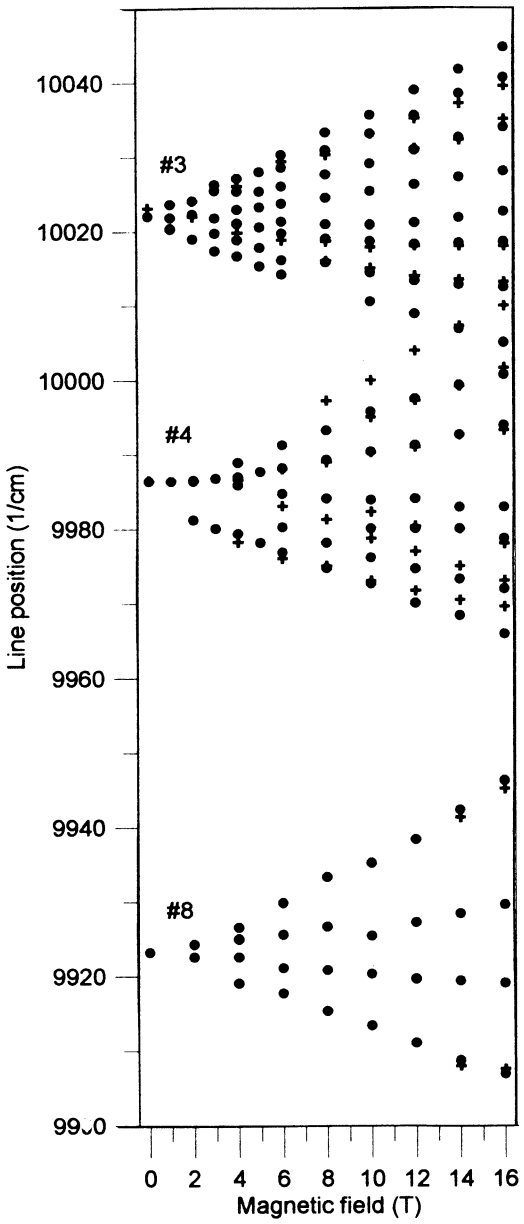

Figure 4. The Zeeman splitting of PL lines #3, #4, and #8 in the <100> (crosses) and the off-axis (circles) oriented sample.

that the two lines, that can be seen for both measurements, are more or less in the same position indicates that no anisotropic g tensor, characteristic for Γ_8, is involved. The observation that the two outer lines are seen in the <100> direction, fixes line #8 unequivocally as the $\Gamma_7 \rightarrow \Gamma_6$ transition. Also the magnitude of the experimentally found Zeeman splitting agrees with the theoretical expectations for this transition, see figure 6, and thus supports such an assignment.

Line #4

Line #4, at about 1001.3 nm was shifted, in the <100> oriented specimen, to higher energies by about 1 cm^{-1}/T, and several lines with low intensity appeared at both sides of it, see figures 3 and 4.
One strong line was seen in the positive polarization and the other ones were of equal intensity up to 8 T. Also in this case the lines with the negative polarization decreased in higher fields, see figure 5. Both samples show slightly different spectra, but at a sufficiently high field always six lines appear, with the total splitting of approx. 5 nm in 16 T. Since line #4 splits in more than four components it is likely to arise from the $\Gamma_7 \rightarrow \Gamma_8$ transition. Only six of the expected eight lines were observed, but the relative splitting and the trend of the lines are in agreement with the theoretical expectations. For the two samples the lines are found in somewhat different positions indicating some anisotropy and, therefore the possible involvement of a Γ_8 level.

The decrease of the intensity of the lines seen in the negative polarization can be explained by the fact that these arise from the higher sublevel of the lowest excited state. The life times for all these forbidden transitions is sufficiently long to obtain an equilibrium Boltzmann distribution. When

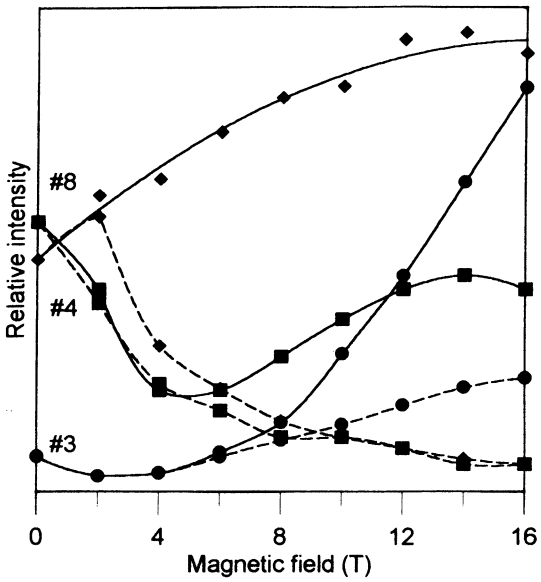

Figure 5. The relative intensities of the PL lines under positive and negative (dashed line) polarizations. The lines are a guide for the eyes.

the field increases the individual levels become differently populated. The fact that exactly half of the lines increases in intensity and the other half decreases indicates that the lowest sublevel of $^2F_{5/2}$ is a Γ_7.

Line #3

Line #3, at about 997.7 nm, was initially not observed at all at zero field; it only became observable at zero magnetic field after the specimen had been exposed to laser light for some time at a high field. The spectrum of this line shows eight components in the off-axis direction and four lines in the <100> direction, yielding a total splitting of about 4 nm in a field of 16 T. In both cases the intensity of *all* lines increases tremendously when the field is increased above 10 T, see figure 4. One line, seen in positive polarization at the lowest energy became four times stronger than the other ones which had approximately equal intensity. Strong circular polarization of the light was detected, see figure 3.

The origin of the lines seen in the "line #3 region" is still unclear.
As discussed before a $\Gamma_7 \rightarrow \Gamma_7$ transition is expected to have two inner lines in the <100> direction and four lines in the off-axis direction, while the intensity of the lines could increase until their splitting is twice the natural line width. This is clearly not the case.
A $\Gamma_8 \rightarrow \Gamma_7$ or $\Gamma_7 \rightarrow \Gamma_8$ transition is expected to have four lines for the <100> direction and eight for the random orientation with the lines in the first case being the inner ones. In contrast, the experiment shows clearly a different pattern of intensities. For an identification with a $\Gamma_8 \rightarrow \Gamma_7$ or a $\Gamma_7 \rightarrow \Gamma_8$ transition there is no reason that all the lines increase in intensity.
Finally, a $\Gamma_8 \rightarrow \Gamma_8$ transition should have 8 and 16 lines when measured for a <100> and a random orientation, respectively. It is possible that not all the lines are observed because of transition probabilities or low occupation of the higher levels. In this case it could also be possible that the lines can only be seen in the higher magnetic field, where the lowest sub-levels of the highest excited state have sufficiently shifted in order to gain population. A $\Gamma_8 \rightarrow \Gamma_8$ transition can, however, not explain the positions of the lines. The fact that identical positions of the lines were found for both samples seems to indicate that the anisotropic Γ_8 is not involved. The fact that both the positively and the negatively polarized lines increase in intensity in higher magnetic field indicates that not the same Γ_7 level is involved as for lines #4 and #8.

In view of the above it is possible that the origin of these lines cannot be found in this energy level diagram and that a different defect is involved. Since in the magnetic field line #3 splits into many

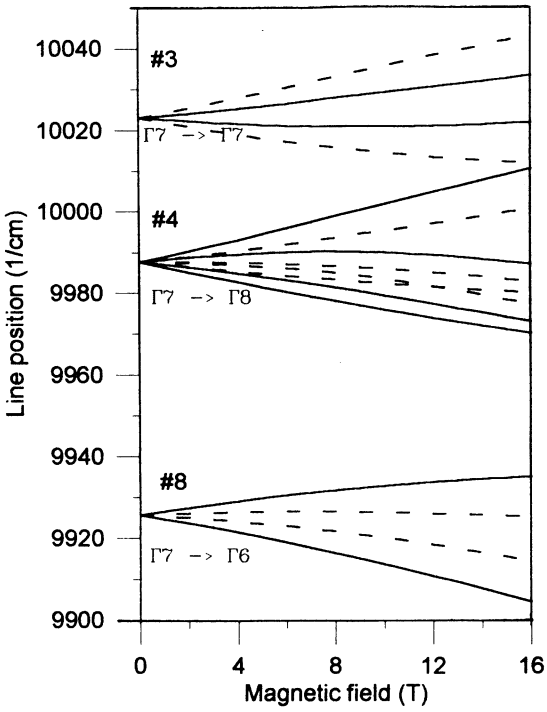

Figure 6. The theoretically expected Zeeman lines, the dashed lines are forbidden in the <100> direction.

components, the symmetry of such a defect should be high, and so it cannot be related to line #1, identified with a trigonal Yb^{3+}_{In} - X_p centre [3].

The fact that for both samples identical intensity of the components, relative to line #4 has been found indicates that line #3 could be connected to the not yet explained lines #5 - #7 and #9 which are always present in the photoluminescence spectrum of InP:Yb with the same relative intensities.

CONCLUSIONS

Based on the Zeeman measurements for lines #4 and #8 it seems reasonable to propose an ordering of levels where Γ_7, and not Γ_8, is the lowest level of the $F_{5/2}$ state. Such a scheme is also in agreement with the crystal field analysis and the expectations that the Yb atom takes a substitutional position on an In site. It can also explain the low intensity of line #3 in the photoluminescence spectrum, since it correspond in this case to the forbidden $\Gamma_7 \nrightarrow \Gamma_7$ transition.

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