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G. Baldacchini, M. Capizzi, M. De Crescenzi, F. Evangelisti and A. Frova: MAGNETIC FIELD EFFECTS ON THE EXCITON AND BIEXCITON IN CdS.

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1. - INTRODUCTION. -

Since the theoretical prediction of the excitonic molecule in 1958[1,2], extensive experimental efforts have been made by various authors to find out the new complex expecially in semiconductors. Unfortunately this kind of investigation proved itself to be a very difficult task. Indeed a clear identification of the emission lines as due to the decay from biexciton states was (and is) not so straight forward as it could be naively thought.

For istance in 1966[3] a new emission in Si was assigned to the decay of the biexciton. Subsequently[4] it was shown that the state responsible of the new emission was a condensate of a degenerate electron-hole plasma, better known today as exciton drops[5].

Up to now the existence of the molecule seems to be well established on sound experimental results and in agreement with the theoretical models only in CuBr and CuCl[6].

In CdS the situation is still controversial. As an attempt to give a more clear picture of the state of the matter, we present in

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Fig. 1 a schematic diagram summarizing the more significant experimental data for CdS taken at low temperatures, mostly at T≃2°K. Rows a, b, c and d display the more typical lines observed by various authors[7,8,9,10,11] in absorption and emission with E⊥c. Rows e, f, and g show the luminescence spectra where biexciton lines (indicated by letters with a star on the top) are supposed to be.

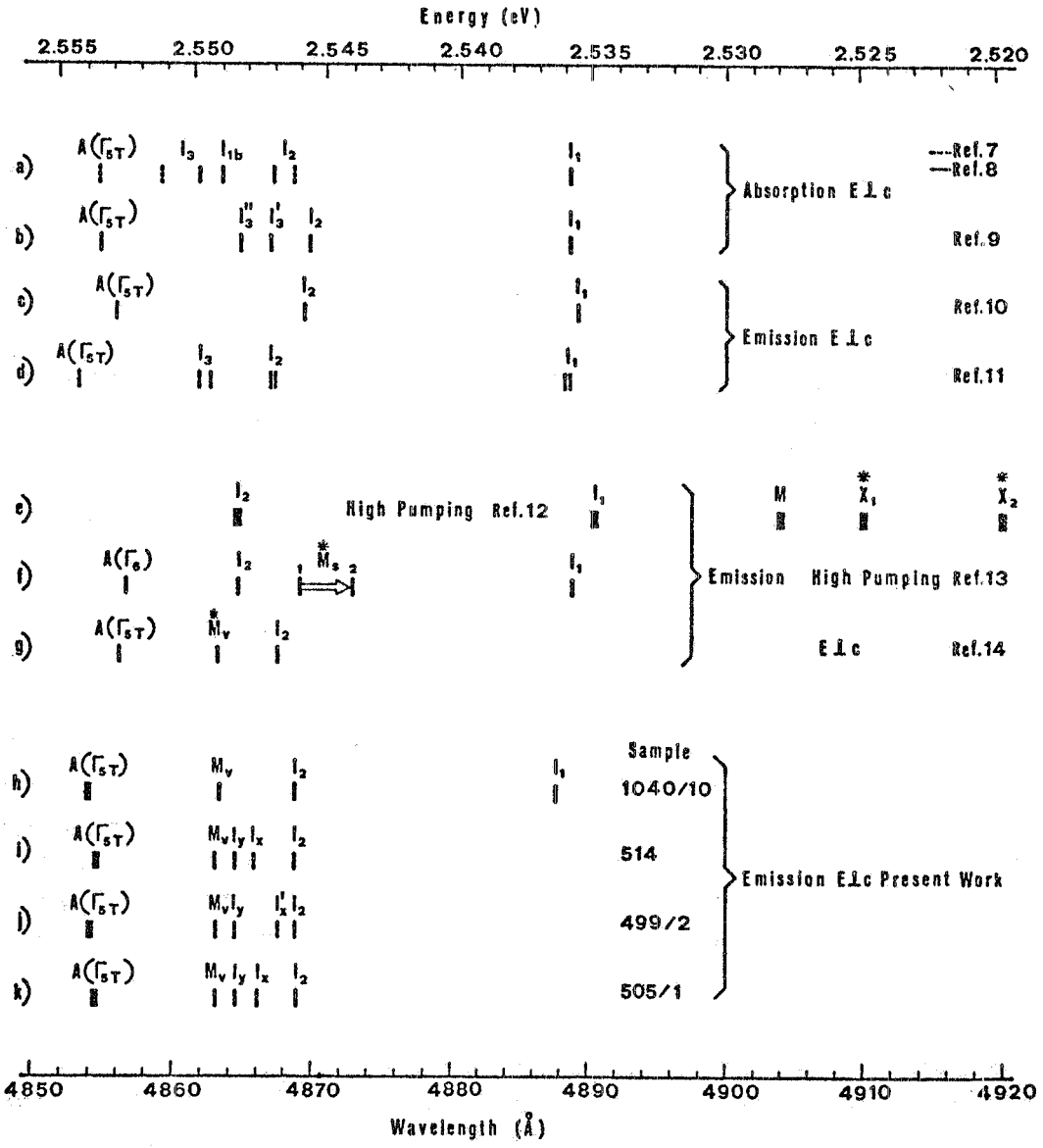

FIG. 1 - Schematic diagram summarizing the data on CdS at T≃2 K. The spectra in a, b, c and d display the more known absorption and emission lines. In e, f and g the letters with a star on the top indicate in the emissions inferred by the authors to some kind of biexcitation decay. In h, i, j, and k the data of the present work are reported to allow a better comparison with the previous ones. The thickness of the markers represents approximately the uncertainty on the position of the lines.

Figueira and Mahr[12] proposed the following model for the line X_1. One exciton of the molecule is excited into the conduction band while the other annihilates emitting a photon. The line X_2 is due to inelastic collisions between two molecules. The molecular binding energy lays between 3 and 4 meV. It is worthwhile to emphasize that both lines emerge from the spectra only at pumping powers higher than 100 kW/cm^2 (26 nsec pulse of 3471 Å radiation).

Shionoya et al[13] observed the line M_S under the excitation of the 3371 Å light (10 nsec pulse) of the Nitrogen laser at pumping rates bigger than 1 kW/cm^2. The position of the line moves from 2.546 to 2.544 eV, 1 to 2 in Fig. 1, while the power is raised from 4 to 40 kW/cm^2. The emission is inferred as due to biexciton decay in a free exciton plus a photon. Taking in account the position of the excitonic triplet state Γ_6, the binding energy results about 5.4 meV.

Voigt and Mauersberger[14] did find a new line, M_V, at 2.5492 eV in very thin samples ($10^{-4} \div 10^{-5}$ cm thickness), pumping with a Hg lamp centerend at 3670 Å; the power was less than 1 W/cm^2. They ascribed the new line to the biexciton decay into a photon plus a free exciton, Γ_6 for $K = 0$ and Γ_5 for $K \neq 0$ (K is the momentum of the molecule). The binding energy, measured from the exciton state Γ_6, is $\sim$3.2 meV.

Recently Jacobson[15] did show that the M_V line develops at high excitation into the M_S line. More precisely the tail of a large band prevails at high density of excitons.

Even more Voigt in a very recent paper[16] showed the existence of two lines at 2.5491 eV, E_1, the previous M_V[14], and at 2.5469, E_2. They can be attributed to two different biexciton decay at low pumping intensity. At high excitation the two lines broaden, and eventually only a large line, whose maximum is shifted towards lower energies is observed. The new emission is identical to the M_S line reported previously by Shionoya[13].

These discoveries seem to reinforce the idea that the molecule really exists in CdS in the range 2.550 ÷ 2.545 eV.

In order to reach a better understanding of the whole matter we performed accurate measurements in CdS under low pumping condition and with a magnetic field up to 80 KG.

In the following after a general discussion on the luminescence and reflectance data taken by some of us previously, we will give in detail the results of the applied magnetic field which remains the main purpose of this note.

2. - PREVIOUS MEASUREMENTS AND INTERPRETATION. -

The experimental investigation was performed on four high--resistivity compensated CdS samples all grown by vapour-transport method, but obtained from two different sources. Sample 1040/10 was supplied by the University of Delaware, the others by General Motors Inc.. The crystals are in form of small platelets a few tens of mm^2 and from 0.2 to 0.5 mm thick. The c axis, lying in the plane, is easily determined by the presence of streaks in its direction.

In Fig. 2, 3a, 3b, 4 and 5 we report the measurements of luminescence and reflectance of the samples immersed in liquid Helium at 1.8 K. All the data refer to the polarization of the light perpendicular to the c axis. We will not describe the experimental apparatus because it is similar to that used for the magnetic measurements, which will be discussed in detail in the next section. Nevertheless we point out that all the previous spectra were obtained by excitation with a 100 W HBO Mercury lamp, focused to give a useful power between 0.5 and 1.5 W/cm^2.

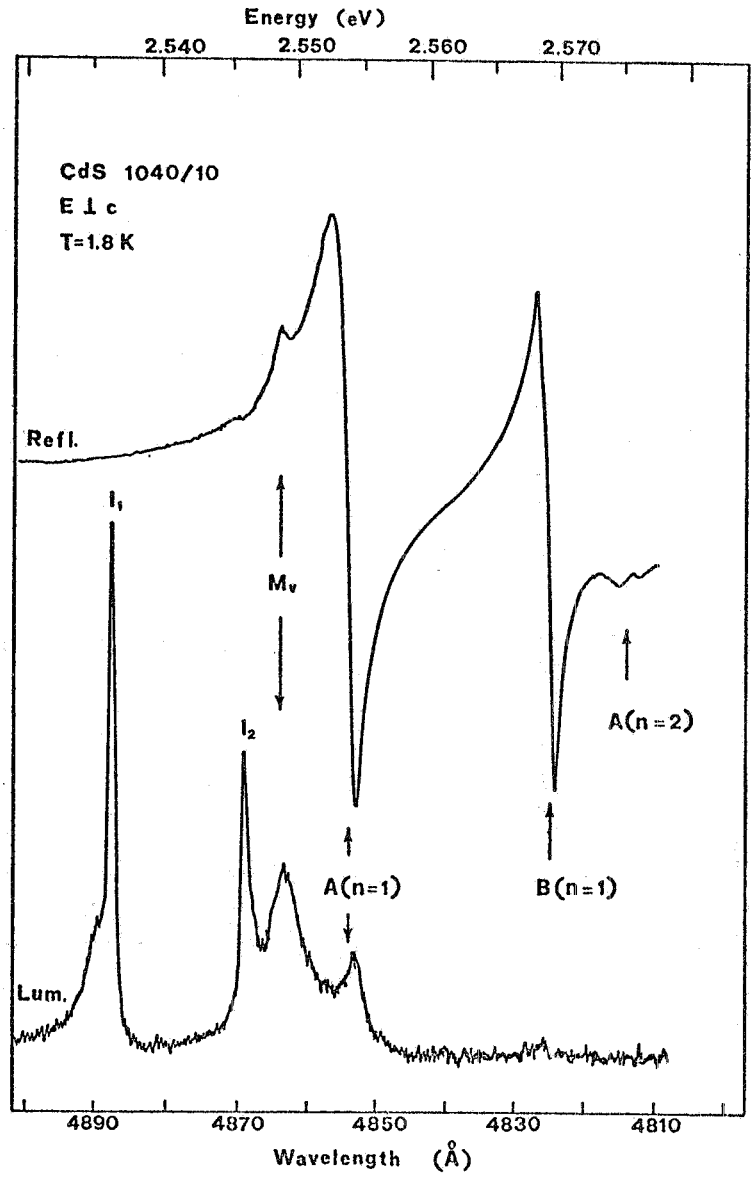

FIG. 2 - Reflectance and luminescence at low intensity pumping: sample 1040/10.

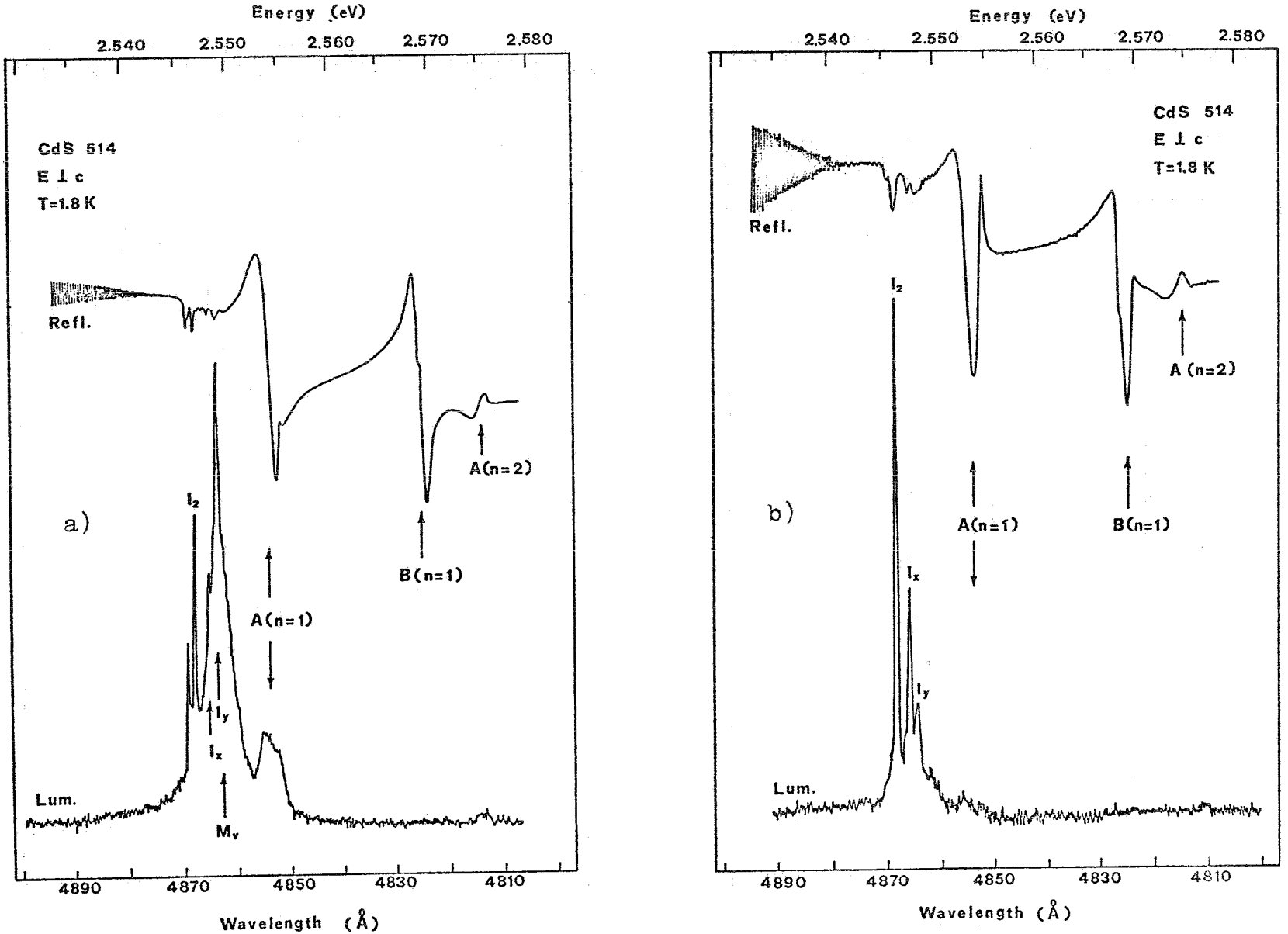

FIG. 3 a, b) - Reflectance and luminescence at low intensity pumping: sample 514. The spectra in b) have been taken one month after those in a.

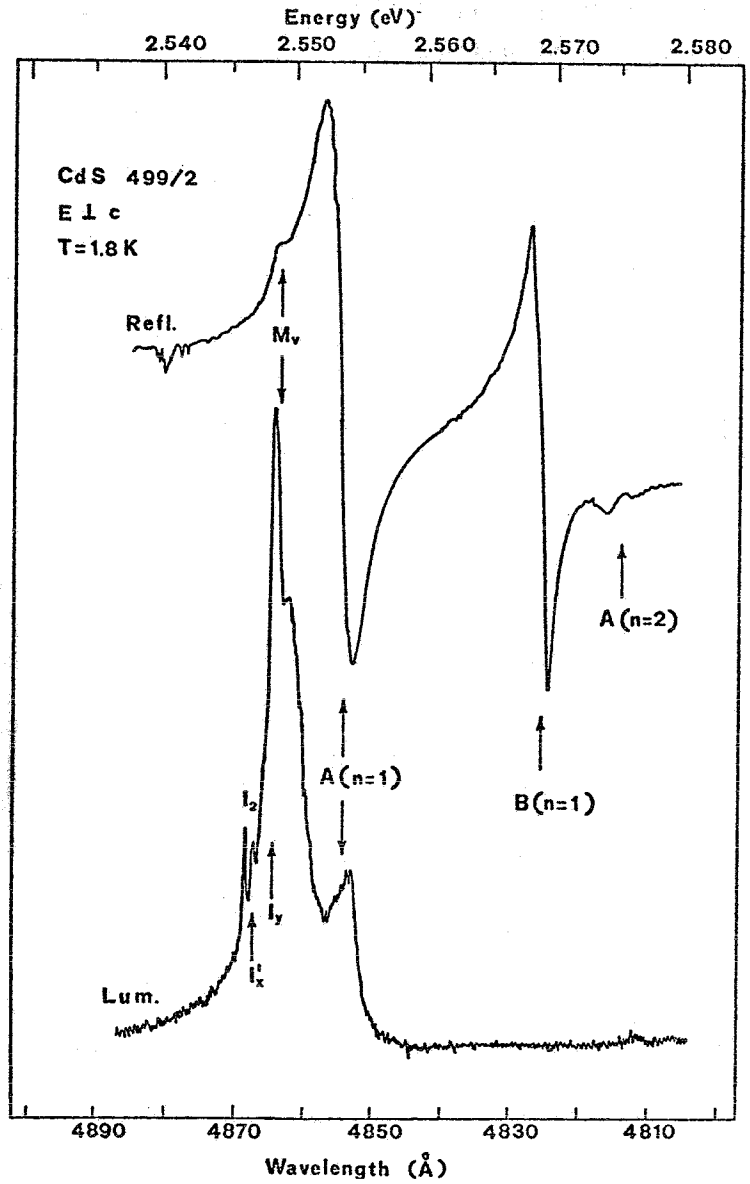

FIG. 4 - Reflectance and luminescence at low intensity pumping: sample 499/2.

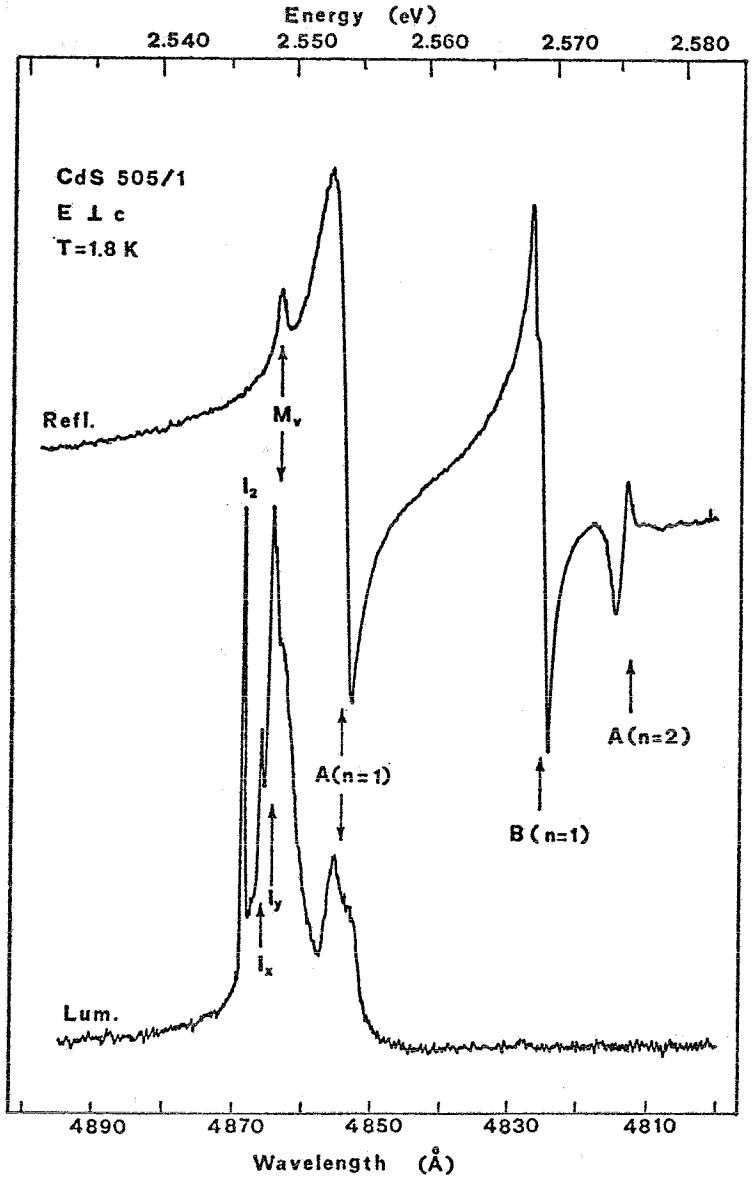

FIG. 5 - Reflectance and luminescence at low intensity pumping: sample 505/1.

In the luminescence spectra (see Fig. 1 where the position of the lines are reported in rows h, i, j, and k) we find the line I_1 (only in 1040/10 sample) due to neutral acceptors (Na or Li), the line I_2 due to neutral donors and the lines I_x, I_y and I'_x, that at a first examination seem to be of the same nature as the I_3 lines due to ionized donors (see rows b and d of Fig. 1). In the same figure we have reported the positions of the center of the structured A-exciton line and the positions of the new emission that we call M_V, because it appears approximately at the same energy of the line seen for the first time by Voigt (row g Fig. 1). This new emission is clearly observable in 1040/10 sample, and it is hidden, except a small shoulder (see Fig. 4 and 5) in the other samples by the I_x, I_y and I'_x lines.

In the reflectance spectra only the intrinsic lines are seen because of the scarce content of impurities in the samples investigated. So the A(n = 1), B (n = 1), and A(n = 2) exciton resonances are clearly displayed. On the low energy side of the A(n = 1) resonance a small bump appears in almost all the spectra at the same position of the M_V line in emission. Trivial experimental check have ruled out the possibility of spurious luminescence signals.

We believe that the M_V line is related to the biexciton molecule in CdS as previously found by Voigt[14]. The following experimental findings support this point of view:

I. The band-width is much bigger than that expected for excitons bound to impurities.

II. It is seen in reflectance where only intrinsic lines are usually observed, no matter how intense are in luminescence the impurity lines.

III. It is not observed in reflectance with pumping monocromatic light. Excitons must exist in the crystal in order to give to the incident photon the opportunity to probe the biexciton state. The reflectance spectra in the previous figures are obtained with incident white light and the reflected beam is analized by a monocromator.

IV. It is strongly polarized $E \perp c$, as requested by the theory[17].

V. Further it is closely related to the A(n = 1) exciton emission intensity.

Indeed, to give evidence to the point V, the M_V emission disappears with the A(n = 1) exciton structure, as it is shown in the luminescence spectra of Figs. 3a and 3b. The two measurements were taken one month apart each other. In Fig. 3a a spike is clearly visible at the longitudinal exciton energy in the reflectance spectra. The spike reveals

the existence of a dead layer due to surface defects[18]. After one month the surface conditions warsened as it is shown by the big spike of Fig. 3b. The dead layer argumented so much that no exciton line is visible in the luminescence. Clearly no biexciton emission could be detected in such conditions. Incidentally the sample 514 has so good and parallel surfaces, that in the spectral region where there is not absorption, below 2.540 eV, a strong interferential effect takes place in form of increasing oscillation while varying the wavelength.

To emphasize further this point we show in Fig. 6 two spectra of the sample 505/1 taken in the same day, (b) after prolonged white light exposure respect to (a). A spike is clearly visible in (b), indicating an increase of the dead layer. As a consequence, the M_V and, less evidently the A(n = 1) (here indicated with F.E.) lines decrease in both the luminescence and the reflectance spectra. The analysis of such a phenomenon was made elsewere[19] and here we wish to point out only the strict analogy between the behaviour of the M_V and A(n = 1) structures.

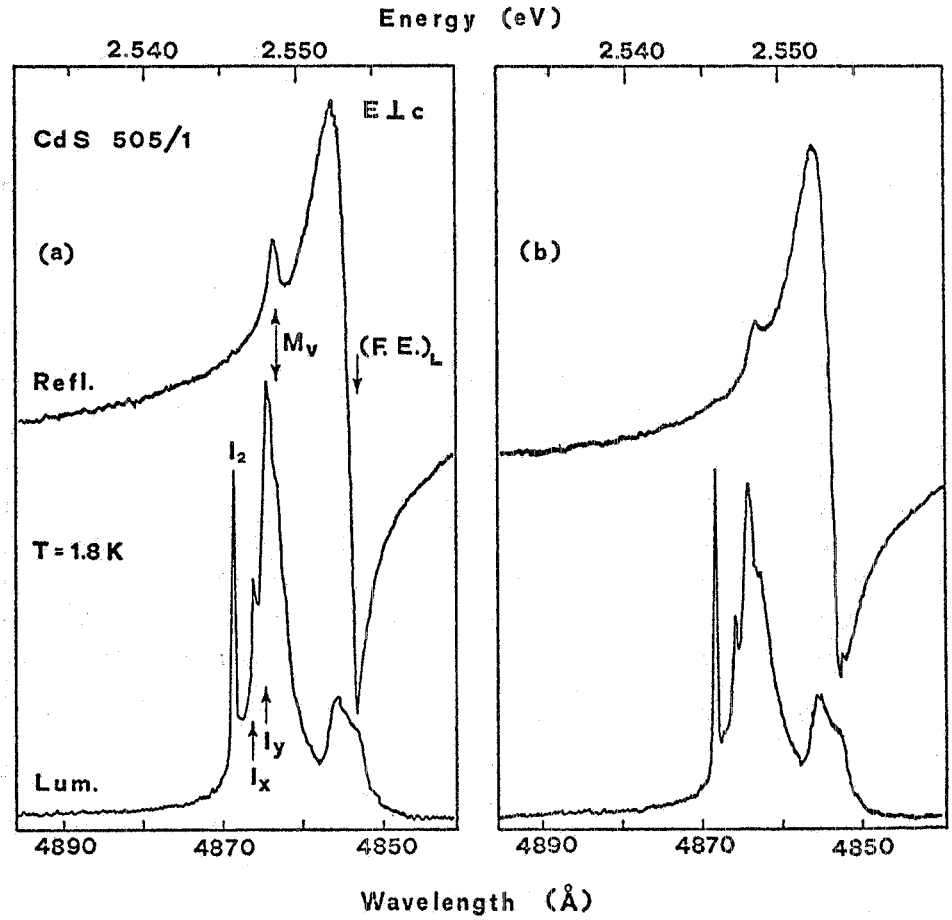

FIG. 6 - Reflectance and luminescence taken the same day but, (b) after prolonged white light exposure: sample 505/1.

At this point of knowledge we have thought that further evidences for the biexciton existence in CdS could be furnished by magnetic field effects.

Indeed because of the Γ_1 symmetry attributed to the molecular ground state[17], no splitting is to be expected for the M_V line. Without entering in the actual debate[16, 17] on the true decay process of the molecule, which would bring us far away from the main purpose of this note, it is interesting to note that if we accept the following process:

$$\Gamma_1^{biex} \rightleftharpoons \Gamma_5^{ex} + h\nu \quad (E \perp c)$$

as the true one, we don't expect any kind of splitting from the final state Γ_5^{ex}. The reason for such behaviour will be clarified in section 4, where we give a detailed analysis on this subject.

3. - EXPERIMENTAL AND RESULTS. -

A block diagram of the experimental apparatus is given in Fig. 7. The CdS crystals described in the previous section were mounted inside a superconducting coil and immersed directly in liquid Helium, pumped below the T_λ point, at ~ 1.8 K generally. With the magnetic optical dewar, described in detail elsewhere[20], it was possible to reach and to maintain for several hours a magnetic field of 80 kG.

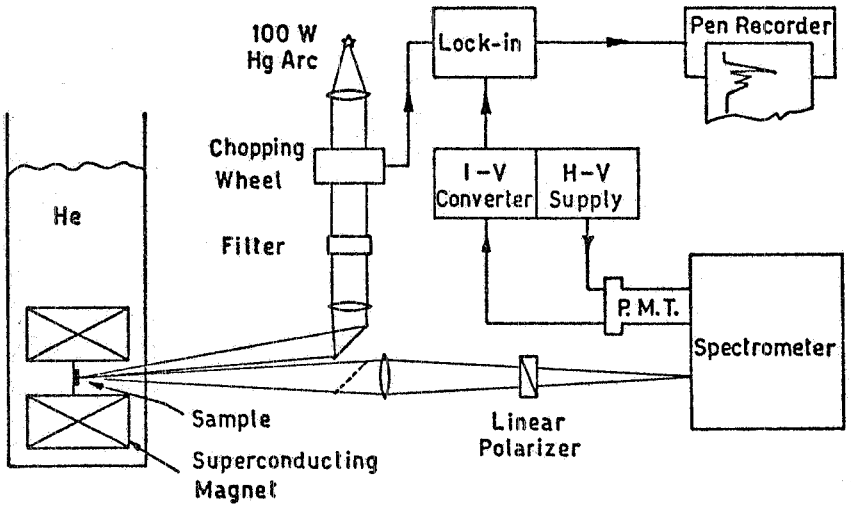

FIG. 7 - Block diagram of the experimental apparatus.

Because of the thickness of the crystals, the luminescence has to be collected on the same side of the pumping light. The radiation of a high pressure mercury lamp, 100 W power, is chopped at ~180 Hz, filtered, and focused on the sample (spot of ~1 mm^2) by means of a good reflecting mirror for luminescence and a 50% trasmitting mirror (dashed line in Fig. 7) for reflectance measurements. The filter used for luminescence measurements is an interferential 450 blue (6197), which cuts at an undetectable level the radiation whose wavelength is longer than 4800 Å. For reflectance we used an interferential filter centered at about 4870 Å with a band-width bigger than 100 Å. In both cases the spot on the sample was focused on the entrance slit of a one meter Gzerny-Turner spectrometer (resolution 8 Å/mm). A lens, $\phi = 5$ cm and $f = 12.5$ cm, is mounted at equal distance, 2f, from the sample and the slit. A linear polarizer, polaroid, chooses the desired status of the light, $E \perp c$ in our measurements. The monochromatic radiation is revealed by an EMI 9558 QB photomultiplier and its current signal transformed in a voltage signal prior to be analysed by a phase sensitive device, i.e. a lock-in amplifier. Eventually its d.c. output is displayed by a common pen-recorder.

In Figs. 8 and 9 we report the recorded luminescence spectra of the samples 1040/10 and 505/1, at various values of the magnetic field. The different spectra, all taken during the same experimental run, are superimposed and shifted vertically for increasing magnetic fields. In this way it is possible to have a complete picture of the magnetic field effects. This kind of measurements were taken for all the samples but we produce here only the previous two, which represent in some way two estreme cases. Indeed the sample 505/1 is very rich of lines, I_2, I_x, I_y, M_v, and A(n=1) while sample 1040/10 has only I_2, M_v and A(n=1), apart I_1. Since in Figs. 8 and 9 it is not easy to follow the behaviours of the A(n=1) structures versus the increasing magnetic field, we show this detail in Figs. 10 and 11. The first one represents only the A(n=1) exciton of the 514 sample and the latter all the spectrum of the 499/2 sample; practically because of the poor resolution this last represents in a correct way only the A(n=1) exciton. In Figs. 12a, 12b, 12c and 12d the positions of the lines or the Zeeman components are given in function of the magnetic field for all the samples.

For the A(n=1) exciton we report in a completely arbitrary way what we believe to be the positions of two lines in the complicated emission structure, see Figs. 9, 10 and 11. As we don't know at the moment the exact nature of these two more or less pronounced lines, we did not draw any solid line connecting the experimental points, as

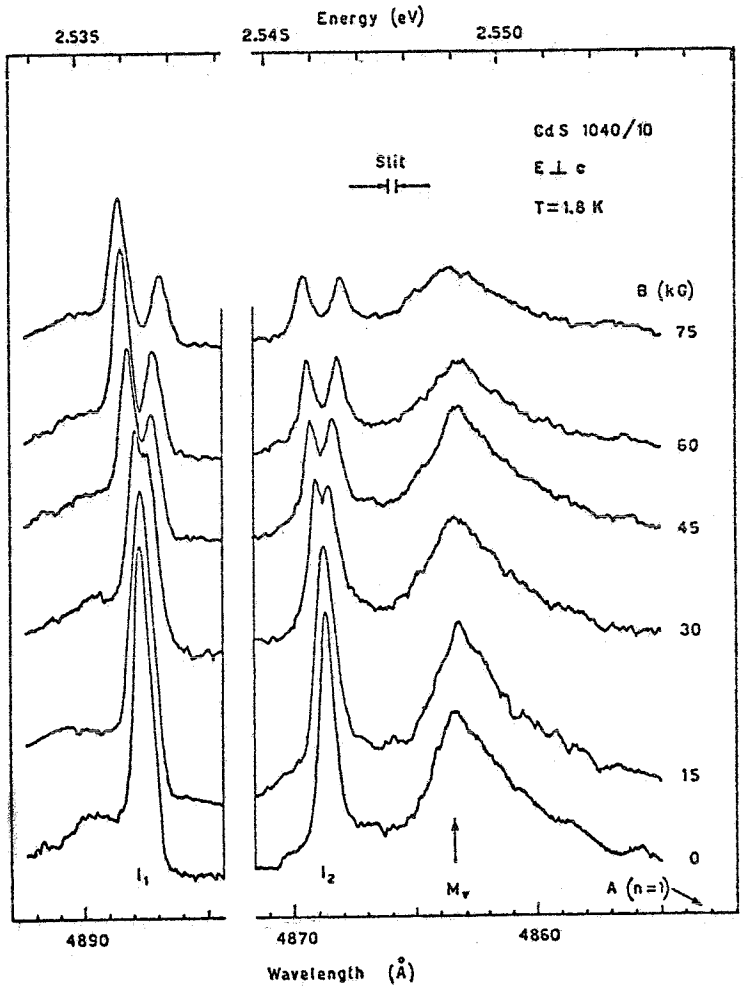

FIG. 8 - Luminescence spectra at various magnetic fields: sample 1040/10.

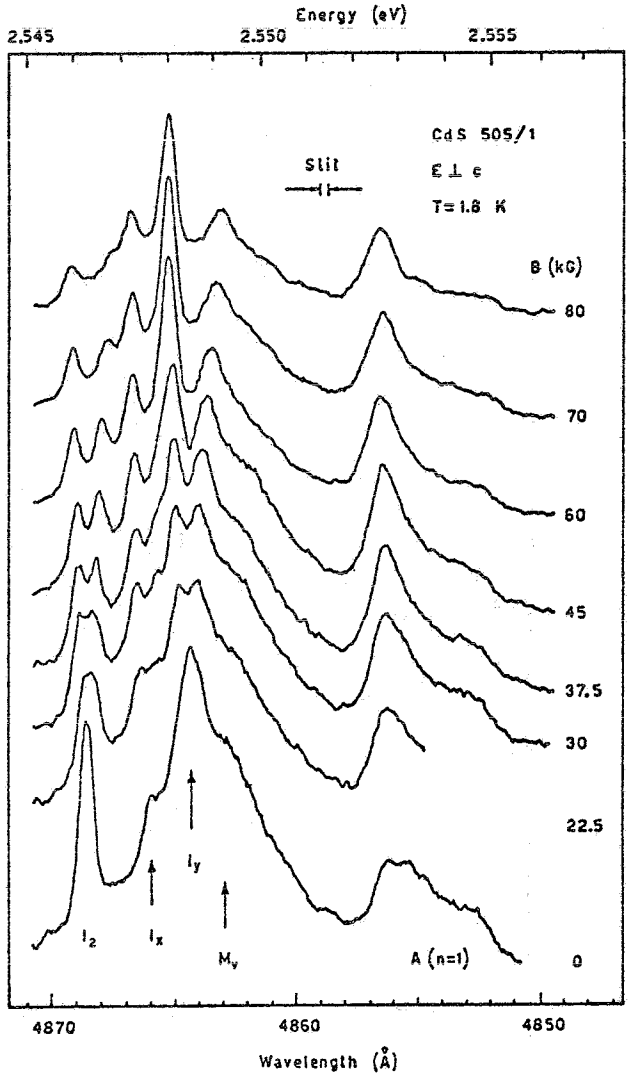

FIG. 9 - Luminescence spectra at various magnetic fields: sample 505/1.

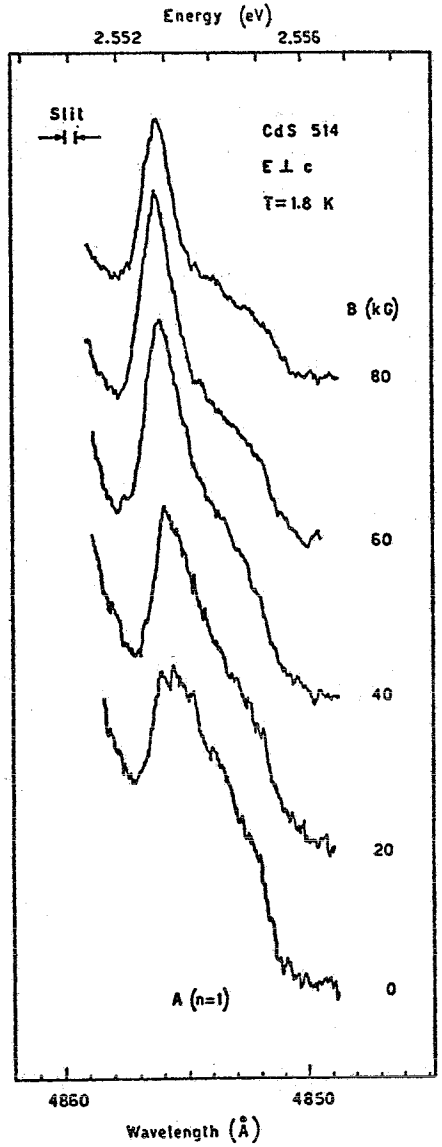

FIG. 10 - A(n=1) exciton emission at various magnetic fields: sample 514.

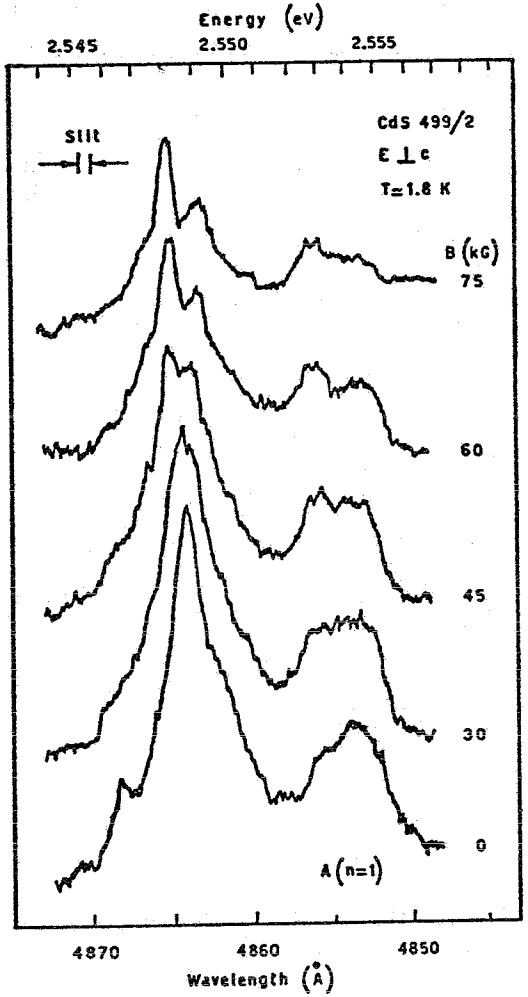

FIG. 11 - A(n=1) exciton emission at various magnetic field: sample 499/2.

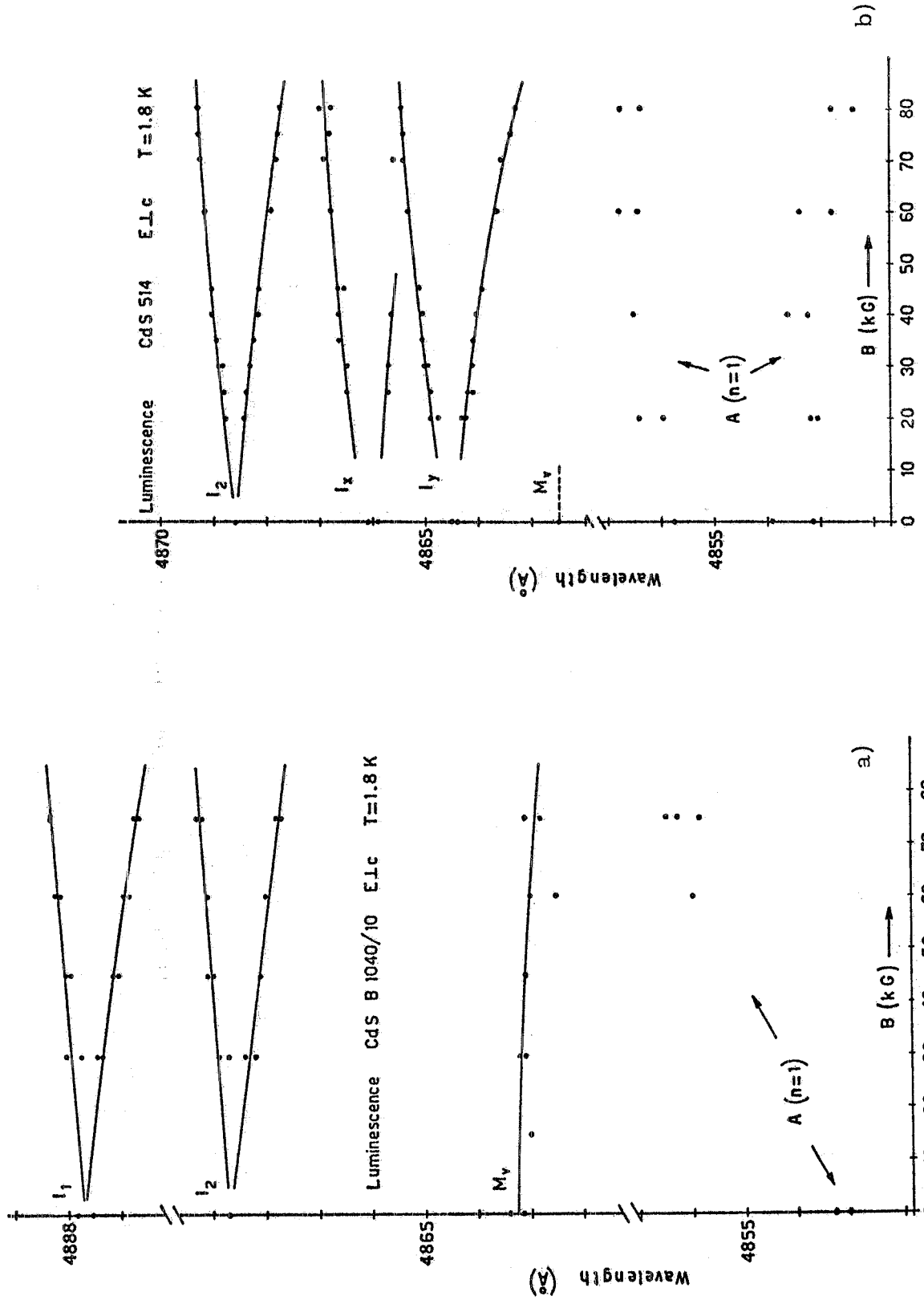

FIG. 12 - Zeeman splittings and magnetic field behaviours of the lines observed in emission: a) sample 1040/10, b) 514.

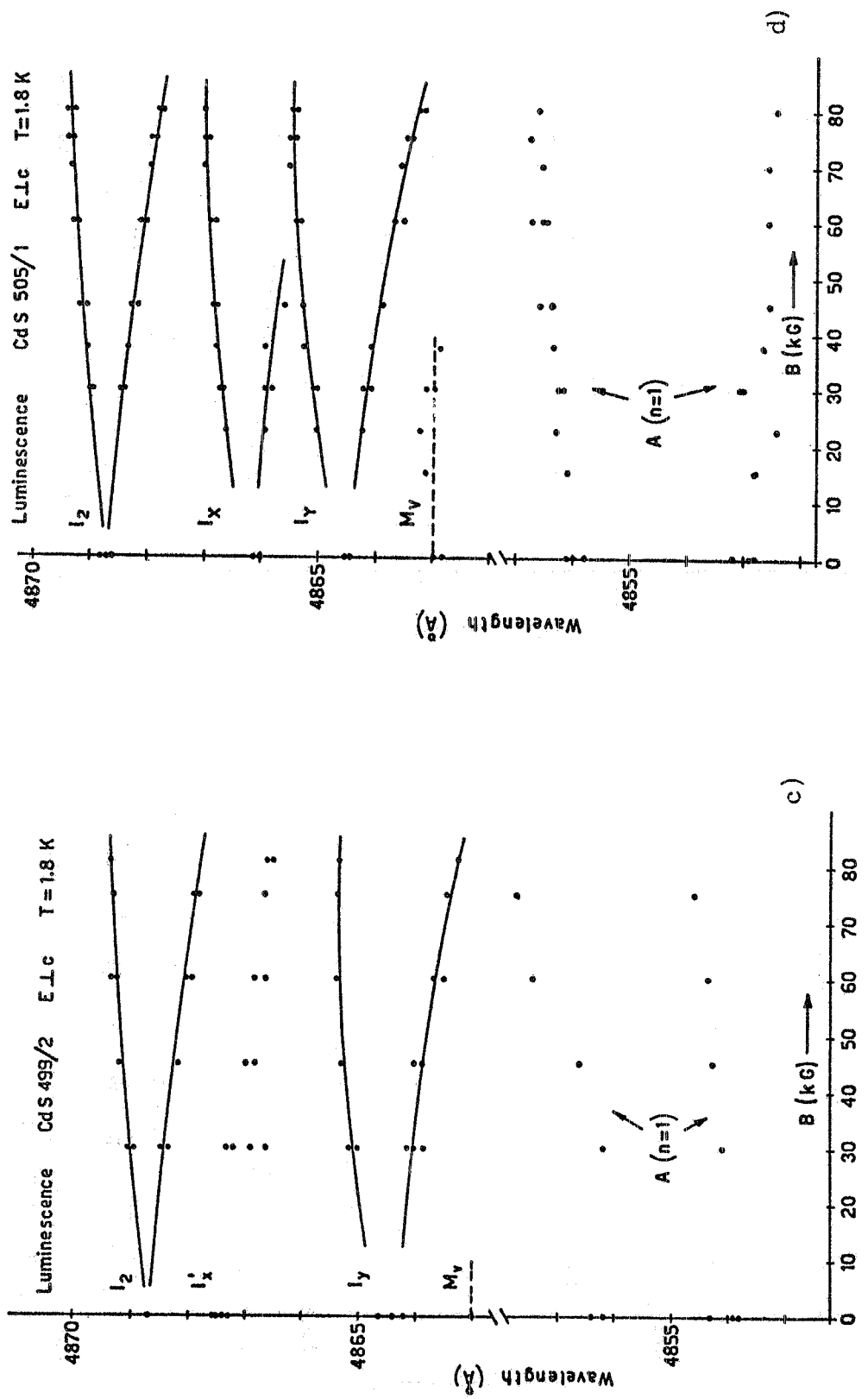

FIG. 12 - Zeeman splittings and magnetic field behaviours of the lines observed in emission: c) 499/2, d) 505/1.

we did for I_1, I_2, I_x adn I_y.

Fig. 13 shows three reflectance spectra taken at different magnetic fields. The typical structures of the A(n=1), A(n=2), and B(n=1) excitons are clearly displayed together with the M_V bump. More detailed spectra of the A(n=1) region for the same sample are given in Fig. 14. In order to have data easier to handle we report in Figs. 15 and 16 the position of the M_V line and the position of the maximum and minimum of the reflectance resonance of the various excitons versus the magnetic field. Fig. 15 refers to sample 505/1 and Fig. 16 to sample 499/2.

Finally a conversion scale, wavelength (Å) → energy (eV) (and viceversa) is drawn in Fig. 17. This enables us to change quickly the wavelength in energy in the region of interest when required.

4. - DISCUSSION. -

In the following we will give the interpretation of the data taken in presence of an external magnetic field. In order to reach this purpose we will use experimental and theoretical data produced by other authors also.

a) Exciton bound to impurities. -

The samples used in this experiment have a purity which represents the maximum obtainable up to date. Nevertheless we have observed the usual impurity emissions, even if not dominant, which are typical of CdS.

The line I_1 is present only in sample 1040/10, see Fig. 2. Until a few years ago it was ascribed to Cd vacancies associated with a donor[10], but recently[21] strong experimental evidence, suggests that it is due to neutral impurities such as Na or Li.

Line I_2, due to a neutral donor[8], is present more (Figs. 2, 3b and 5) or less (Fig. 4) pronounced in all samples. In particular in sample 514, Fig. 3a, two I_2 lines, 1.2 Å apart, were seen in one experimental run. This fact is clearly bound to the other peculiar properties of this sample, which we have discussed in section 2. With the resolution used through the experiments, 0.25 Å at best, we cannot resolve the eventually present doublet nature of I_1, 0.3 Å, and I_2, 0.2 Å, which has been observed sometimes[22, 11].

The lines I_y, I_x and I'_x, observed in samples 514, Figs. 3a and 3b, 499/2, Fig. 4, and 505/1, Fig. 5, seem to be of the some nature of the lines I_3, see Fig. 1, seen by various outhors in absorption[7,8,9] and emission[11]. They are normally attributed to ionized donors.

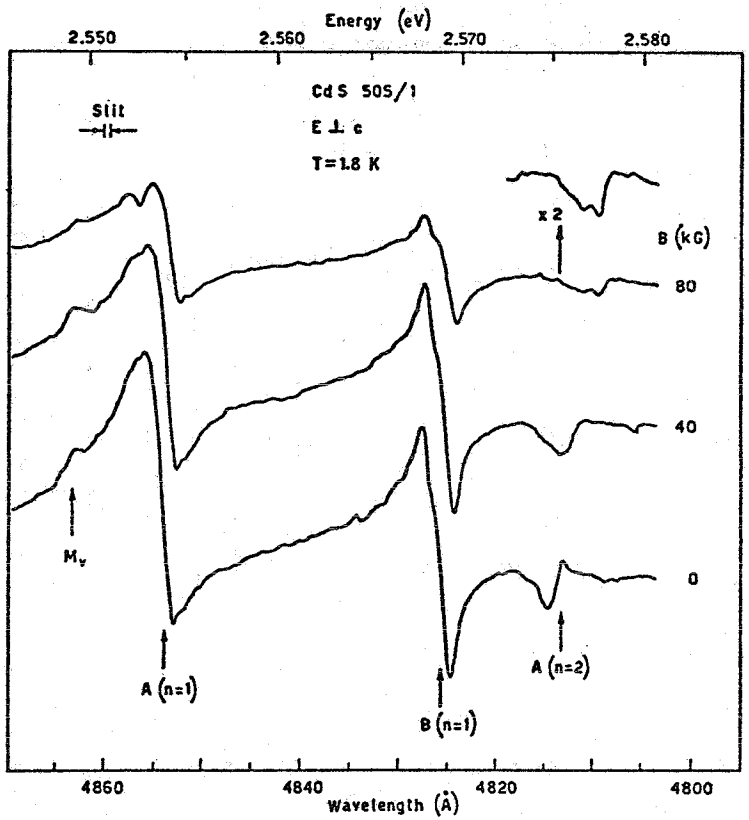

FIG. 13 - Reflenctance spectra over a wide spectral region at various magnetic fields: sample 505/1.

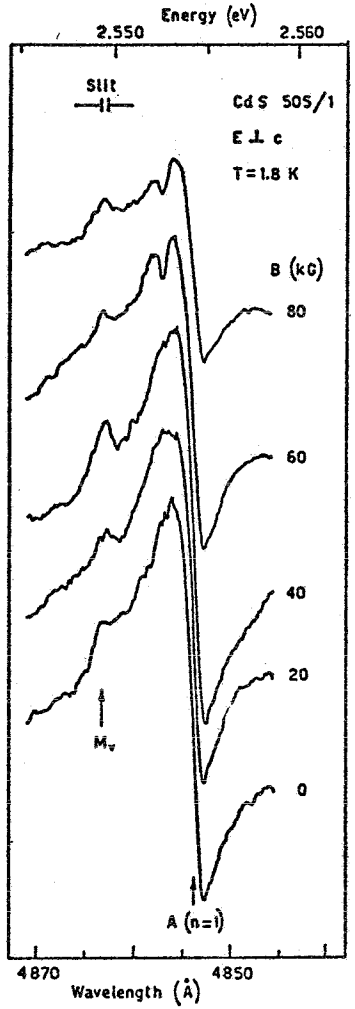

FIG. 14 - Reflectance around A(n=1) structure at various magnetic fields: sample 505/1.

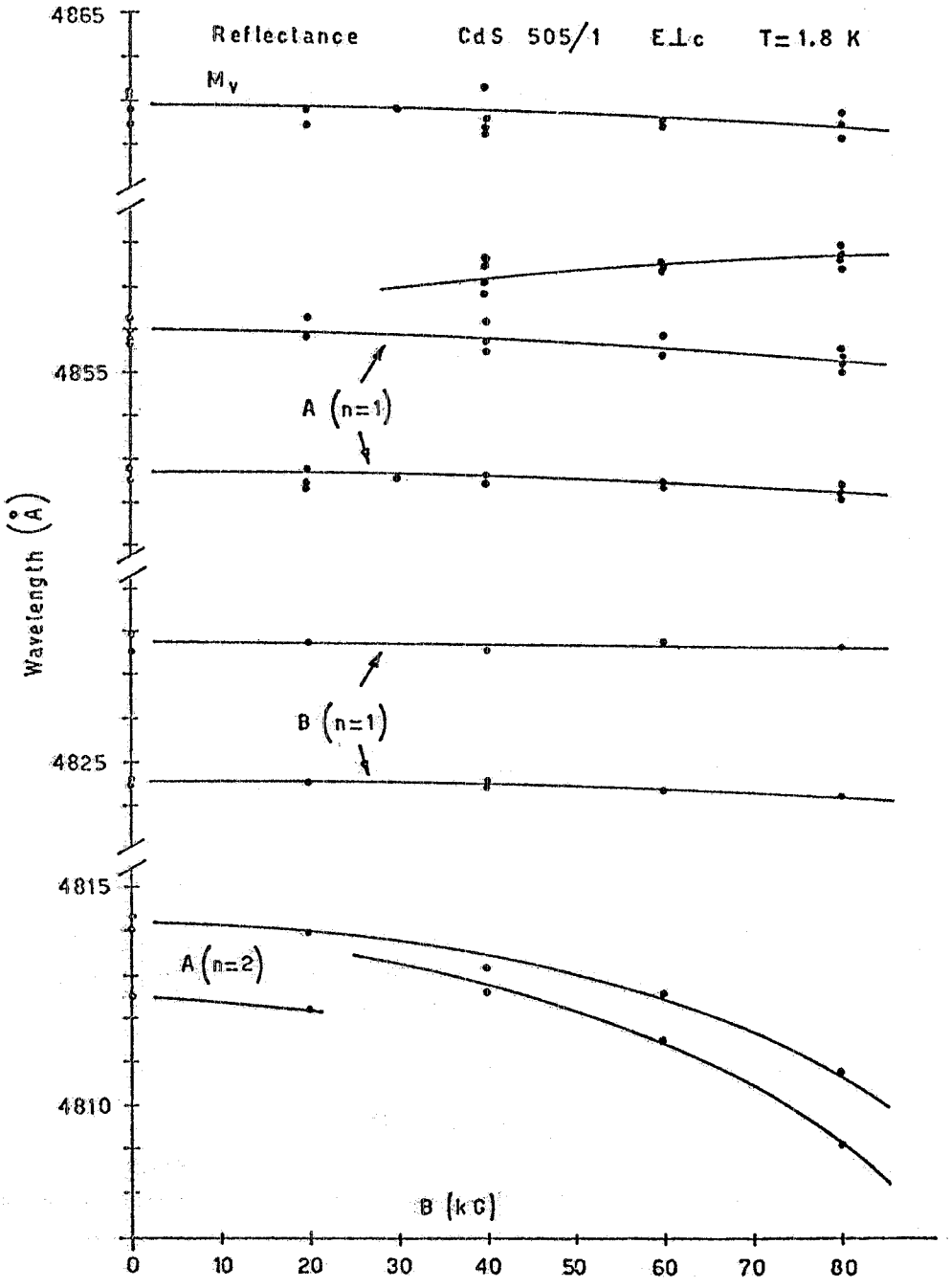

FIG. 15 - Magnetic field dependence and splitting of the structures observed in reflectance: sample 505/1.

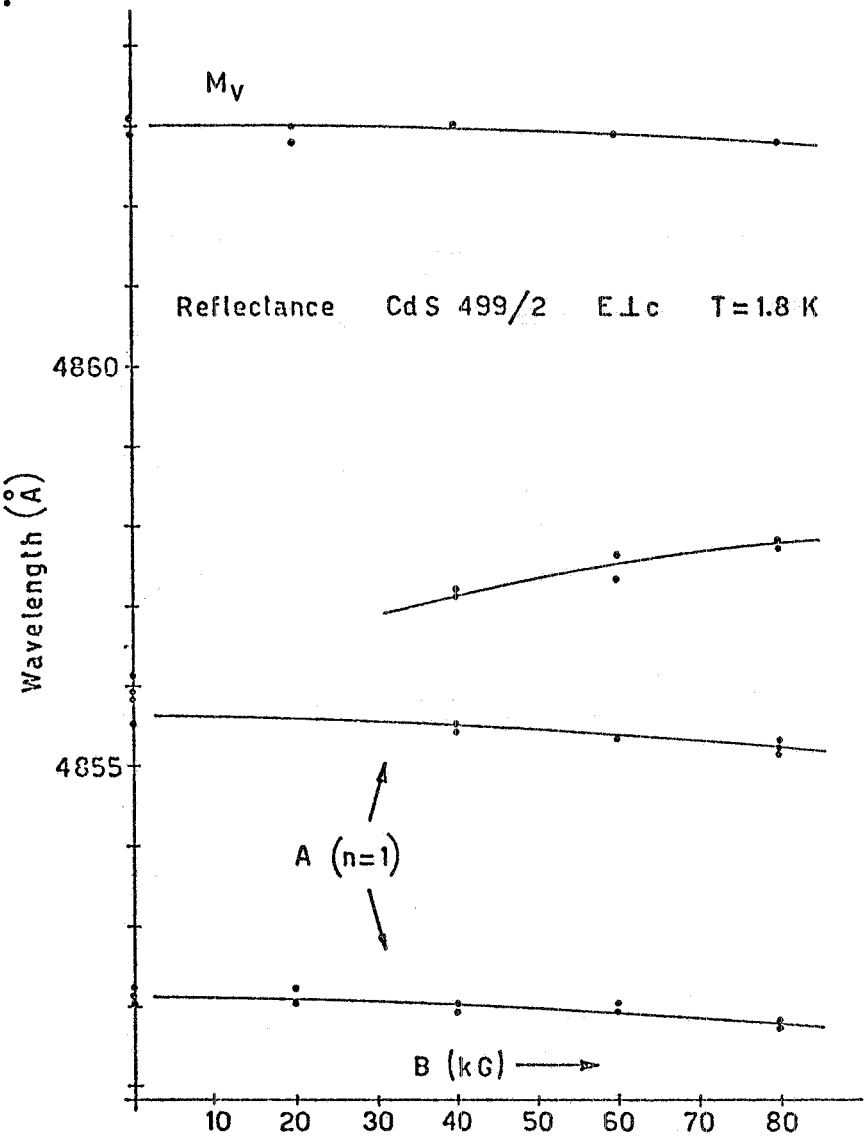

FIG. 16 - Magnetic field dependence and splitting of the M_V line and A(n=1) exciton in reflectance: sample 499/2.

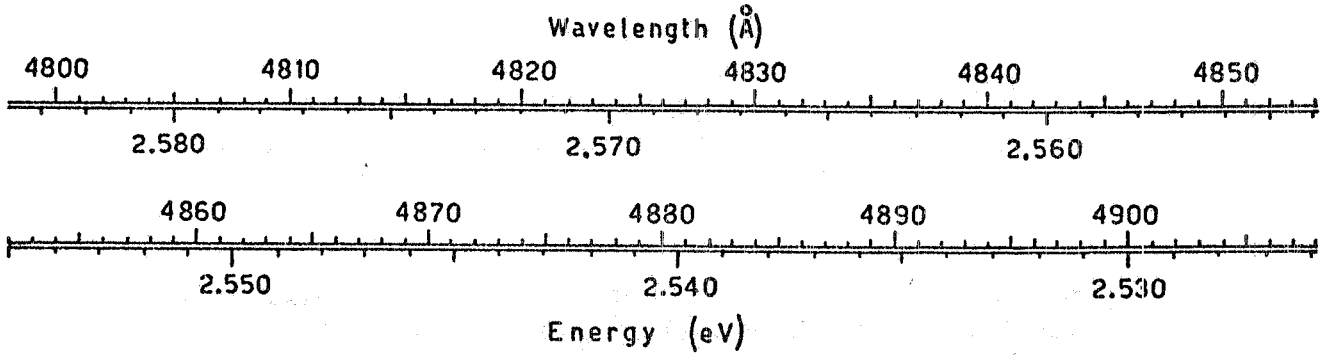

FIG. 17 - Conversion scale wavelength (Å) ⟷ energy (eV) in the region of interest.

By means of accurate measurements versus the magnetic field, as in the Figs. 8 and 9, it was possible to extract the data reported in Figs. 12a, b, c and d, and eventually the g-factor and the diamagnetic shifts.

The experimental g values for I_1 is 1.96 ± 0.08 to compare with the expected values 1.80[10] and 1.76[23]. Assuming a quadratic shift with the magnetic field of both the Zeeman components, $\Delta\nu = a^2B^2$, we have $a \simeq +1.5 \times 10^{-10}$ cm^{-1}/gauss^2, which is in complete disagreement with the value $a = -9 \times 10^{-10}$ cm^{-1}/gauss^2[23].

For the I_2 lines we have a mean value $g = 1.81 \pm 0.07$ against 1.76[10], while the diamagnetic shift is practically non-existent in all samples but 1040/10, for which $a = +1.3 \times 10^{-10}$ cm^{-1}/gauss^2.

As we pointed before, lines I_x, I_x' and I_y, because of their position in the spectrum, seem to have the same origin as the lines I_3, which are produced by ionized donors. The relative intensity of the two Zeeman components of the I_y line, see Fig. 9, indicates that the magnetic separation comes from the excited state as expected[8]. Besides the experimental splitting is fitted much better with the law, $[\Delta^2 + (gB)^2]^{1/2}$, than with the linear one, gB.

From the experimental point of view we cannot arrive at any conclusion for the I_x' line, because only one Zeeman component is observable. The other is completely hidden by the much intense I_2 line.

The I_x lines have a mean g-factor of 1.78 ± 0.07 and a separation in zero field $\Delta = (0.30 \pm 0.05)$ meV, which compare fairly well with $g \simeq 1.7$[8] and $\Delta = 0.31$ meV[8, 11]. Instead we have observed a small diamagnetic effect, $a \simeq +1.4 \times 10^{-10}$ cm^{-1}/gauss^2, never observed before. Unfortunately it was not possible to make a very accurate magnetic analysis of the I_x lines, because they are partially hidden by the more intense I_y lines.

The I_y lines have $g = 2.35 \pm 0.10$ and $\Delta \simeq (0.28 \pm 0.05)$ meV. The separation in zero field is in fairly good agreement with the previous data, but the g-factor is in disagreement with all the known experimental results and theoretical analysis[8]. Also a small diamagnetic effect is present, $a \simeq +1.7 \times 10^{-10}$ cm^{-1}/gauss^2, never observed before.

At moment we cannot explain this anomalous big g-factor and it is clear that more detailed measurements would be necessary in order to clarify the whole situation. For istance a better resolution would be highly desirable to establish if both the Zeeman components

exist in zero field. Indeed the lines I_3 seem to have the peculiarity to show only the high energy Zeeman component in zero field[8], even if both components have been revealed in some cases[11]. From our measurements only the high energy component seems to exist in zero field, but we cannot make this statement with absolute certainty.

b) A-exciton. -

The exciton state A(n=1) in CdS is composed by two levels doubly degenerate with symmetry Γ_6 and Γ_5.

The plitting comes out from the exchange interaction between the electron and the hole. Commonly the previous states are known as triplet, Γ_6, and singlet, Γ_5, because of the spin value, S = 1 for Γ_6 and S = 0 for Γ_5. However this simple picture is not true, because the spin-orbit interaction mixes the triplet and singlet states in such manner that only two doubly degenerate states remain eventually, as stated before.

The optical transitions are always forbidden for Γ_6, and allowed for Γ_5 only with $E \perp c$.

The A(n=1), Γ_5, exciton has been observed experimentally both in reflectance and in luminescence and the typical structures are shown in Figs. 2, 3a, 3b, 4 and 5. In Fig. 1 the positions of the emission line of the A(n=1) transverse exciton, Γ_{5T}, are given in the rows h, i, j and k. In the other rows of the same Figure we report the position of the states Γ_5 and Γ_6 as extracted by the experimental work of various outhors.

The shape of the line in luminescence changes with the sample, but a two-line structure, not resolved, seems to be present in all the samples. Till now the true origin of this kind of structure is not known. Nevertheless the more reliable models are essentially the following two.

In one the authors[24] propose that the double structure in the emission is due to the lower and upper polariton branch, in which the complex exciton(Γ_5)+photon splits itself as a consequence of their reciprocal interaction.

In the other model[25] only the lower polariton branch gives a substantial contribute to the luminescence and the peculiar structure is ascribed to the reflectivity of the emitted light on the crystal-vacuum surface.

When an external magnetic field is applied the degeneration of the states is removed and new optical transition rules are to be applied. To have an idea on what is going to happen, it is enough to utilize the

general results of the group theory.

The magnetic field is perpendicular to the crystal axis, i. e. $B \perp c$. In this geometrical configuration the group of symmetry of the whole Hamiltonian is C_s, which belongs to the bigger group of symmetry of the CdS crystal, C_{6v} The C_s group contains two elements, the identity and the reflection on a plane normal respect to the magnetic field. In the new representation the Γ_5 state can be reduced as in the following:

$$\Gamma_5(C_{6v}) \rightarrow \Gamma_1(C_s) + \Gamma_2(C_s)$$

and like wise for the Γ_6 state:

$$\Gamma_6(C\quad) \rightarrow \Gamma_1(C_s) + \Gamma_2(C_s)$$

In the dipole approximation the interaction has the symmetry properties of Γ_2 for E//B and Γ_1 for $E \perp B$. Because the ground state of the crystal has the symmetry of Γ_1 and:

$$\Gamma_1 \times \Gamma_2 = \Gamma_2 , \qquad E//B$$

$$\Gamma_1 \times \Gamma_1 = \Gamma_1 , \qquad E \perp B$$

we can easily deduce that one component of both Γ_5 and Γ_6 states is always observable in optical transition in presence of a magnetic field. We would like to remind at this point that the Γ_6 state is a forbidden state in absence of a magnetic field.

The previous analysis tells us nothing about the intensity of the various lines and the mixing of the old states. In order to have some details in this respect we have to make an analysis taking into account the magnetic field as a perturbation.

This kind of perturbation has the symmetrical properties of the $\Gamma_5(C_{6v})$ for $B \perp c$. This means that the matrix element of the perturbation between the singlet and triplet states, $\langle \Gamma_5 | \mathcal{H}'(B) | \Gamma_6 \rangle$, is not zero. Indeed one has:

$$\Gamma_6 \times \Gamma_5 = \Gamma_3 + \Gamma_4 + \Gamma_5$$

Hence the forbidden triplet state Γ_6 mixes itself with the singlet state Γ_5 and becomes partially allowed in an external magnetic field. As a consequence the intensity of the optical transitions to and from the Γ_6

state will increase with the magnetic field.

Our experimental data of reflectivity, Figs. 13 and 14, show the onset of a new peak on the low energy side of the maximum of the normal reflectivity. Because it appears only in an external magnetic field, we believe that it is due to the normally forbidden Γ_6 state, or better to one of its components. The position of this new maximum versus B is reported in detail in Figs. 15 and 16. A linear shift toward the low energy side of the spectrum is easily observed. By extrapolation in zero field it is possible to obtain the value of the exchange splitting between Γ_6 and Γ_5, which is ~ 0.4 MeV. This value is in agreement with the experimental data found by other authors.

The new emission allowed in a magnetic field is observed in the luminescence spectra also (Figs. 10 and 11). Its features are mainly an increase and a shift of the exciton structure on the low energy side of the spectrum (see for istance Figs. 12a, b, c, d). We would like to remind that an analogous behaviour has been observed in luminescence with the configuration $B//c$[26].

c) Biexciton. -

From the experimental spectra in luminescence, Fig. 8, and in reflectance, Fig. 13 and 14, no detectable splitting is observed on the line M_V up to 80 kG. This result is a further proof which leads to the excitonic molecule picture. Indeed, as stated in section 2, no splitting has to be expected in a magnetic field for the ground state of the molecule, which has Γ_1 symmetry. It is necessary to point out that the magnetic field opens a new way of decay for the molecule. Indeed the triplet exciton state Γ_6 is now partially allowed, but the oscillator strength associated with the new transition is small compared to the allowed one through the state Γ_5. It is clear that in such condition it is not possible to observe the new decay in the broad structure of the M_V line.

At this point it would be possible to make other considerations, but they have been the object of a detailed analysis appeared in a recent paper[19] to which we refer.

5. - CONCLUSIONS. -

The main purpose of this note was to verify the biexciton nature of the line M_V with the help of an external magnetic field. In order to clarify the previous point it was necessary to study the behaviour of the whole edge emission and reflectivity in CdS. Clearly the few data on the A(n=2) and B(n=1) excitons (Figs. 13 and 15) have been reported here only for sake of completeness.

The previous analysis was rewarding for the very interesting results obtained. The splitting of the lines I_y, bigger than expected, the small diamagnetic shifts, and the strong dependence of the A(n≠1) exciton structure on the magnetic field, are a few examples. Especially in the latter case it would be highly desiderable to make more experiments with different geometrical configuration in order to have a better understanding of its polaritonic nature.

As for as the biexciton is concerned it is clear that we have reached a better belief on its existence. But is is necessary to stress that the debate is still in progress. Indeed during the completion of this note new papers appeared on the scientific literature. In one[27] the existence of the molecule M_S is confirmed using the uniaxial stress technique. In other two, the first one[28] using one-photon absorption and the second one[29] two-photon absorption, no evidence is observed which can be attributed to the formation of free excitonic molecules.

In conclusion it is clear that this kind of studies is of paramount interest in the physics of the semiconductors and lot of work has still to be made in order to have a more complete picture of the basic phenomena included.

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