Angular-dependent magnetoluminescence study of the layer compound $2H$-PbI_2

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The near-band-gap recombination radiation of the layer compound $2H$-PbI_2 is studied in magnetic fields up to 18 T from 1.7 to 40 K. The principal bound exciton (BE) splits anisotropically and shows a small diamagnetic shift in magnetic field. On the basis of these results the binding center of the BE is identified as being a neutral donor. According to the pseudoacceptor model for (D^0,X) bound excitons the isotropic g value of the hole, $g_h = -0.4$, is equal to the g value of the valence band. The diamagnetic shift allows the determination of the free-hole mass to be $m_h = 0.195\ m_0$. This is the first determination of these band-structure parameters for PbI_2, and gives the effective-mass acceptor binding energy $E_A = 71$ meV, which is shown to be at the same time an upper limit for the excitonic binding energy. The anisotropic bound-electron g values are deduced to be $g_\parallel = -1.4$ and $g_\perp = -2.1$. The sign and size of the parameters determined agree well with predictions of band-structure theory. The free exciton shows an angular-dependent shift to lower energy with increasing magnetic field. This is shown to be due to a linear Zeeman splitting of the A_3^- exciton state, the upper split level becoming depopulated with magnetic field due to thermalization. Exciton g values $g_{ex}^\parallel = 1.0 \pm 0.5$, $g_{ex}^\perp = 2.0 \pm 0.5$ are found. From this the free-electron g values are deduced to be $g_{el}^\parallel = 1.4 \pm 0.6$, $g_{el}^\perp = 2.4 \pm 0.6$. By comparing the spectra obtained at zero magnetic field for $\vec{k}$ parallel and perpendicular to $\vec{c}$, the splitting of the A_3^-, A_2^- exciton levels is derived to be $\lesssim 0.8$ meV.

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I. INTRODUCTION

There is little detailed experimental knowledge of the electronic energy bands and the resultant optical properties in the region of the fundamental band gap in $2H$-PbI_2. A series of free-exciton lines has been observed in this region at ~2.5 eV.[1] However, the series has in the past been interpreted in a number of conflicting ways with excitonic Rydbergs ranging from 15 to 140 meV being proposed.[2] Recent magnetoabsorption measurements were in favor of a larger binding energy, a lower limit for the excitonic Rydberg of 180 meV on an isotropic model being obtained.[3] Difficulties in the study of these lines are caused by their relatively large linewidths, of the order of 5 meV (in absorption) for the more-highly-excited states. The large linewidths are caused partially by the considerable number of stacking faults present even in the best quality samples of this layer material and also by the lifetime broadening arising from the large longitudinal-transverse splitting of the exciton (6.2 meV for the $n=1$ state for $\vec{k} \| \vec{c}$).[4] Similar stacking-fault arguments apply for the case of the bound excitons where nevertheless somewhat narrower linewidths of the order of 2 meV are obtained.

In this paper the first magnetoluminescence studies of bound excitons in $2H$-PbI_2 are reported. It is shown that by working at 1.7 K and in magnetic fields up to 18 T linear Zeeman splittings of the bound exciton line at 4974 Å can be observed and relevant electron and hole g values deduced, leading to a direct determination of the free-hole g value. Evidence is presented that the exciton is bound to a neutral donor with ~ 5-meV binding energy. A diamagnetic shift of the bound exciton line of 0.2 ± 0.1 meV to higher energy is found between 0 and 18 T. This allows a value of 71 meV for the acceptor Rydberg to be deduced on the basis of a pseudoacceptor model for (D^0,X). The consequences of this diamagnetic shift for the value of the free-exciton binding energy are discussed. In addition a shift of the free-exciton ground state of ~1 meV to lower energy is found in the present measurements and enables the exciton and free-electron g values to be determined.

The paper is organized as follows. In Sec. II a survey of the band structure and symmetries of the lowest conduction band and top valence bands in $2H$-PbI_2 is given. Then in Sec. III the experimental setup and the results obtained are described. This is followed in Sec. IV by an analysis of the experimental Zeeman splitting of the bound exciton on the basis of the group-theoretical selection rules expected for an exciton bound to a neutral impurity. In Sec. V the variation of the Zeeman splitting with angle is described. Then in Sec. VI the diamagnetic effects of the bound exciton are discussed. This is followed in Sec. VII by the results for the free exciton, and finally in Sec. VIII the main findings of the paper are summarized.

II. BAND STRUCTURE OF $2H$-PbI_2

The $2H$ polytype of PbI_2 has the hexagonal CdI_2 structure with space group D_{3d}. The electronic

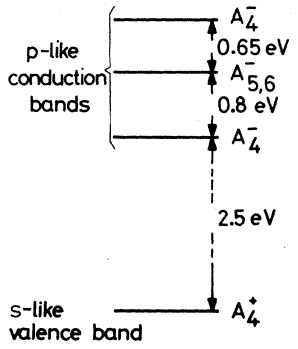

FIG. 1. Schematic illustration of the conduction and valence band energy levels in $2H$-PbI_2 at the A point of the Brillouin zone.

band structure has been calculated using the empirical pseudopotential method by Schlüter and Schlüter[5] and by Doni *et al.*[6] using a tight-binding approach. They show that the minimum band gap occurs at the surface of the Brillouin zone at the A point, which is, however, group-theoretically equivalent to the Γ point. These authors[5,6] find that when crystal-field and spin-orbit interaction effects are included, the three lowest conduction bands are of A_4^-, $A_{5,6}^-$, and A_4^- symmetry as shown in Fig. 1. The band splittings given in Fig. 1 are those obtained from optical-reflectivity measurements.[7] The results of these calculations imply that the excitonic absorption at the fundamental band edge will be cationic with the conduction-band states arising predominantly from Pb, 6p atomic orbitals and the valence band states from Pb, 6s orbitals. The existence of cationic 6s character at the valence band edge has been shown by Harbeke and Tosatti[2] to be essential to explain the behavior of exciton lines in the $Pb_{1-x}Cd_xI_2$ alloy system as a function of x and also to explain the large negative pressure coefficient of the $n=1$ exciton line in PbI_2.

Recent photoemission measurements by Margaritondo *et al.*[8] have confirmed that "strong cation s character" is present in the valence band, although from another photoemission experiment Azoulay and Ley[9] have proposed that the top valence band has a more important iodine 6p character in a Pb, 6s –I, 6p hybridized state, at the same time pointing out, however, that only the Pb, 6s character would be important for the electric-dipole-allowed excitonic one-photon transition.

III. EXPERIMENTAL RESULTS

For low-temperature measurements the crystals under study were directly immersed in liquid He at 1.7 K. Measurements at higher temperatures up to 30 K were taken using a He-gas flow cryostat. The luminescence was excited by 4579-Å light from an Ar^+ laser and the emitted radiation dispersed by a 1.5-m Jobin-Yvon spectrometer and detected with a cooled photomultiplier. The crystals used for this work were Bridgman grown and were of thickness ~1 mm. They were prepared in the Ecole Polytechnique Fédérale, Lausanne, by Dr. F. Levy and were kindly donated by him. No electrical data related to the impurity concentration are known. Measurements could be

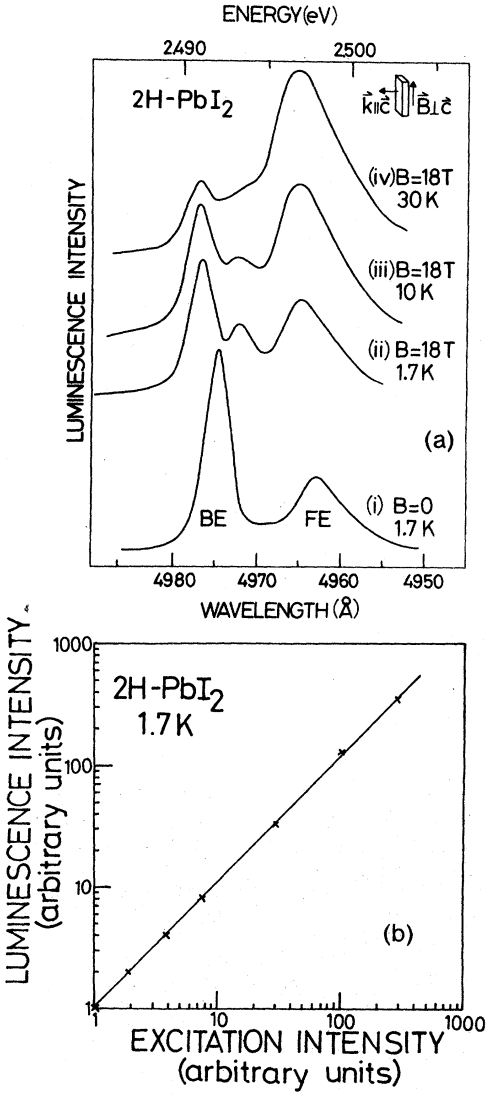

FIG. 2. (a) Luminescence spectra observed from the face of the crystal $\vec{k}\parallel\vec{c}$ with (i) magnetic field $\vec{B}=0$ at 1.7 K; (ii) $\vec{B}=18$ T in the Voigt configuration $\vec{k}\perp\vec{B}$; (iii) same as (ii) but at 10 K; (iv) same as (ii) but at 30 K. The line labeled FE is the free exciton, BE is the bound exciton. (b) Variation of luminescence intensity of BE line at 4974 Å against the exciting laser intensity (I_{exc}). $I_{exc}=1$ unit corresponds to ~1mW of incident power.

taken in both Faraday and Voigt configurations (and at intermediate angles) in magnetic fields up to 18 T.

Curve (i) of Fig. 2(a) shows the luminescence spectrum for light emitted with electric vector $\vec{E}\perp\vec{c}$ at zero magnetic field and at 1.7 K. The spectrum is of similar quality to that reported in the earlier studies of Levy *et al.*[10] The weaker of the two observed lines (FE) is that arising from the free exciton while the stronger of the two (BE) at 4974 Å arises from an exciton bound to an impurity. The position of the free-exciton line (4963 Å) agrees with that obtained from absorption studies on the 2*H* polytype.[2] Levy *et al.*[11] and Kleim and Raga[12] have also shown that the temperature dependence of the two lines with the free exciton becoming much stronger and broader above ~30 K and the bound exciton much weaker is consistent with the interpretation of the lines as arising from free and bound excitons respectively. Similar behavior can also be seen from the present measurements in Fig. 2, where the crystal temperature was raised up to 30 K in connection with the search for thermalization of the Zeeman components obtained for magnetic field $\vec{B}\perp\vec{c}$.

In order to establish conclusively whether line BE arises from an exciton bound to a neutral or ionized impurity, the effect on the luminescence spectrum of curve (i) of Fig. 2 (a) of additional, below band-gap light from a He-Ne laser at 6328 Å was investigated. It was found that application of 6328-Å light caused a reduction of ~10% (for 1-mW incident power at 6328 Å and 1 mW at 4579 Å) of the intensity of the bound exciton line, compared to its intensity without the additional illumination, all other experimental conditions being the same. Care was taken that both lasers were focused on exactly the same spot on the sample. This result shows that line BE arises from an exciton bound to a neutral center, since the below-band-gap light must reduce the number of neutral centers present in the crystal by ionizing by them. The opposite effect, i.e., an increase in intensity, would be expected if line BE arose from an exciton bound to an ionized center. Since the energy of the He-Ne laser was far above the ionization energy of the binding center, it is clear that the quenching of the luminescence will not be too pronounced. Similar methods to identify the charge state of a binding center were employed by Thomas and Hopfield[13] in their early work on bound excitons in CdS.

The intensity of the bound exciton line was found to increase as a linear function of the exciting laser intensity over a range of more than two orders of magnitude as shown in Fig. 2(b). This indicates that the exciton is bound to a majority center since these are the centers that in the absence of external illumination are neutral. If the binding were to a minority center, the creation would occur as a two step process and one would expect at least at low excitation levels a superlinear increase, as was observed, e.g., for the case of the (A^0,X) recombination in GaAs:Sn.[14]

Curve (ii) of Fig. 2(a) and Fig. 3(a) show the spectra at a magnetic field of 18 T for $\vec{B}\perp\vec{c}$ and $\vec{B}\parallel\vec{c}$ and with $\vec{k}\parallel\vec{c}$.

Considering the case of $\vec{B}\perp\vec{c}$ first, a splitting of the bound exciton line into two components is observed. A small shift of the center of gravity of the two lines of 0.2 ± 0.1 meV to higher energy was also found. The weaker component [see curve (ii) of Fig. 2(a)] could only be detected at fields greater than 11 T. At 18 T the splitting was equal to 4.4 Å (2.2 meV). No polarization of the lines was found. In addition a 1-meV shift of the free exciton line to lower energy and a broadening was found. The effect of raising the sample temperature up to 30 K is also shown in curves (iii) and (iv) of Fig. 2(a). No variation of the relative in-

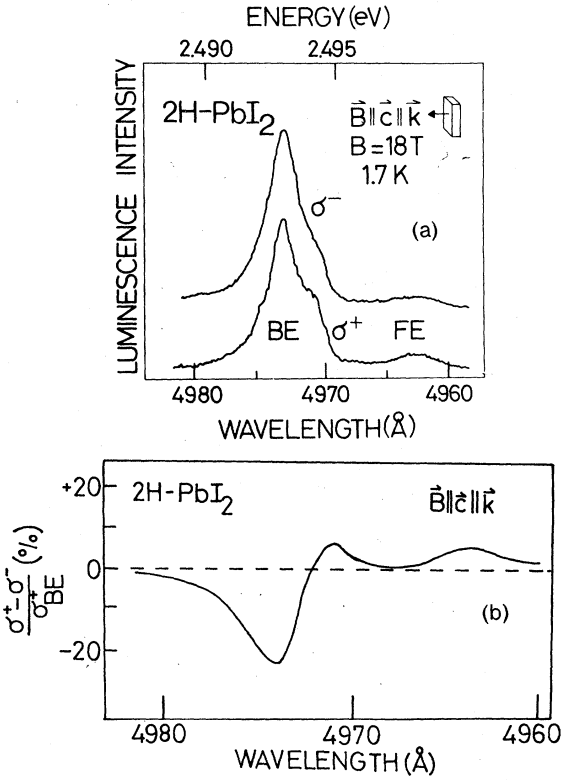

FIG. 3. (a) Magnetoluminescence spectrum at 18 T in the Faraday configuration $\vec{B}\parallel\vec{k}\parallel\vec{c}$ at 1.7 K. The light was observed from the face of the crystal. (b) Circular polarization of the spectra presented in Fig. 3(a), as represented by $(\sigma^+-\sigma^-)/\sigma^+_{BE}$, plotted against wavelength. σ^+_{BE} is measured at the peak of BE at 4974 Å.

tensities, i.e., no thermalization of the Zeeman-split components was observed up to the temperature where bound exciton features disappeared.

For $\vec{B}\parallel\vec{c}\parallel\vec{k}$ the bound exciton line again splits into two components (with a smaller splitting of 1.1 meV at 18 T) as shown in Fig. 3(a). These are found to be circularly polarized as indicated in Fig. 3(a) and more easily visible in the plot of $(\sigma^+-\sigma^-)/\sigma^+_{BE}$ given in Fig. 3(b). The polarization of the two lines into σ^+, σ^- is only partial but this is probably due to depolarization effects occurring because of the number of internal reflections taking place before the light leaves the crystal. Similar effects have been observed in the luminescence of bound excitons in GaP.[15] The σ^+ component of the free exciton line is shifted by 0.5 meV to lower energy from the $B=0$ position. Its σ^- component is considerably weaker.

Finally in Fig. 4 the spectrum obtained for $\vec{B}\perp\vec{c}$ but the light observed from the edge of the crystal, i.e., $\vec{k}\parallel\vec{B}$ is shown. The main bound exciton line BE again splits into two components but with a splitting of 3.6 Å (1.8 meV) at 18 T.

Two other notable features are observed in this configuration. First, a subsidiary bound exciton feature is observed at ~1.5 meV lower energy than BE. This line shifted by ≃0.5 meV to lower energy in a magnetic field of 18 T but was found to decrease in intensity by a factor of ~3 between 0 and 18 T. This feature was not observable in all crystals studied but when it was observed it was found in the same energy position as in Fig. 4. The behavior of this subsidiary peak will not be discussed further in this paper.

Second, the free exciton line was found at ~0.8 meV lower energy than for $\vec{k}\parallel\vec{c}$ (at $B=0$) and shifted by an additional 0.3 meV to lower energy between 0 and 18 T.

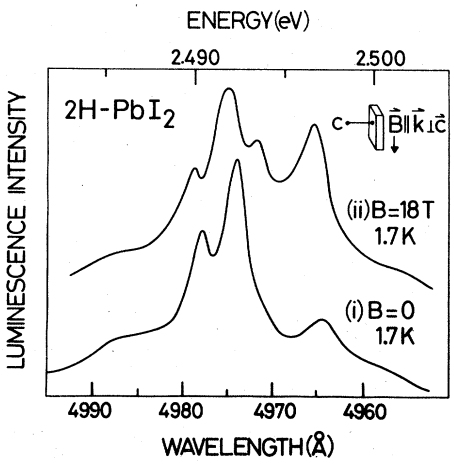

FIG. 4. Magnetoluminescence spectra at 1.7 K (i) $B=0$, (ii) $B=18$ T in the Faraday configuration $\vec{B}\parallel\vec{k}$ with $\vec{k}\perp\vec{c}$. The light was observed from the edge of the crystal.

IV. GROUP-THEORETICAL SELECTION RULES AND ANALYSIS OF EXPERIMENTAL SPLITTINGS

The magnetic field results given in Sec. III will now be analyzed in terms of the group-theoretical selection rules expected for the recombination of an exciton bound to a neutral center in $2H$-PbI_2.[16]

In Fig. 5 it is shown that if the exciton is bound to a neutral donor (the reverse arguments apply if it is bound to a neutral acceptor) then the initial state is holelike, the two electron spins being paired antiparallel to fulfill the requirements of the Pauli exclusion principle. The complex then transforms in the same way as an unpaired hole. The final state of the transition is a single electron transforming as A_4^- in D_{3d}.

The electron states contributing to the exciton will be mainly from the lowest conduction band transforming as A_4^- since the next conduction band is 0.8 eV higher in energy (Fig. 1) whereas the excitonic Rydberg is in the range 0.05–0.2 eV. Therefore for the purposes of the present work the contribution from higher bands can be neglected.

It was explained in Sec. II that the valence and conduction bands in PbI_2 are composed predominantly of s- and p-like atomic orbitals, respectively, at least so far as an electric dipole transition between them is concerned. To a reasonable approximation then, and for the purposes of analysis of the present experimental results, the

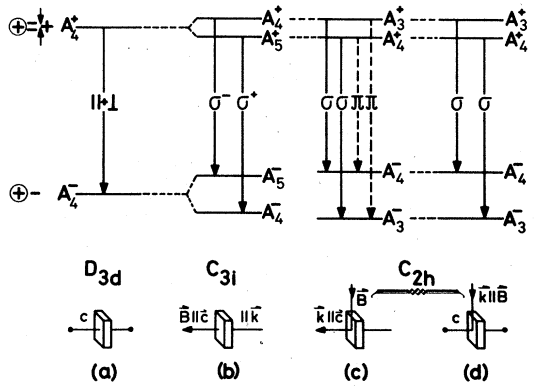

FIG. 5. Energy levels of an exciton bound to a neutral donor (D^0,X) and of a neutral donor D^0 and the dipole-allowed selection rules between the two derived on the basis of group theoretical arguments for (a) $\vec{B}=0$, (b) $\vec{B}\parallel\vec{c}\parallel\vec{k}$, (c) $\vec{B}\perp c$, $\vec{k}\parallel\vec{c}$, and (d) $\vec{B}\perp\vec{c}$, $\vec{B}\parallel\vec{k}$. For reasons explained in the text the ordering of the Zeeman split levels in the initial state is opposite to that in the final state. π and σ refer to the magnetic field as axis.

g factor for holes (g_h) in the uppermost valence band can be taken as approximately isotropic, whilst the g value for electrons will be of the form $g_e = (g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta)^{1/2}$, where θ is the angle between the magnetic field and the c axis.[13]

For a magnetic field parallel to the c axis (group C_{3i}) the A_4^+, A_4^- levels split into A_4^+ and A_5^+ and A_4^- and A_5^-, respectively, and for light polarized in the layer planes, i.e., the Faraday configuration ($\vec{k} \| \vec{B} \| \vec{c}$) one σ^+ and one σ^- transition are expected. For $\vec{B} \perp \vec{c}$ (group C_{2h}) the levels split into $A_3^+ + A_4^+$ and $A_3^- + A_4^-$, respectively, and for light polarized once again in the layer planes ($\vec{k} \| \vec{c}$) two σ and two π transitions are allowed. Finally, if luminescence is observed from the edge of the crystal with the light polarized perpendicular to the layer planes $\vec{B} \perp \vec{c}$, $\vec{B} \| \vec{k}$ two σ transitions are observable. All these results are summarized in Fig. 5, where the transformation of the levels for the different configurations discussed above and the group-theoretically allowed transitions are indicated.

The experimental results can be explained consistently on the basis of the above model by taking the splitting of the initial state to be small. This explains the experimental observation of only two lines in Fig. 2 where each line must consist of an unresolved unpolarized doublet. For the other configurations only two transitions are in any case observable. In addition, if the initial-state splitting is small, no thermalization effects will be observable. The lines for $\vec{B} \| \vec{c}$ will, however, still be polarized $\sigma^{+,-}$. Since the σ^+ line in Fig. 3 appears at higher energy than the σ^- line, the electron g value must be negative [see Fig. 5(b)].

The nature of the binding center and electron and hole g values will now be discussed. The splitting for $\vec{B} \perp \vec{c}$ is a factor of $\simeq 2.0$ higher than for $\vec{B} \| \vec{c}$ (both $\vec{k} \| \vec{c}$) (the behavior between these two extreme directions will be discussed in Sec. V) and thus it is clear that the final state of the transition has an anisotropic splitting and so must be a single electron. The binding center must then be a neutral donor, the initial state of the transition being (D^0, X)

Since the splitting at 18 T for $\vec{k} \| \vec{B} \perp \vec{c}$ (1.8 meV) is less than the splitting for $\vec{k} \| \vec{c}$, $\vec{B} \perp \vec{c}$ (2.2 meV) although the magnetic field direction relative to the c-axis is the same in both cases, it can be seen by reference to Fig. 5 and that the splitting of the π lines is greater than that of the σ lines. This implies that the spectroscopic g values in the initial and final state have opposite signs. Assuming that the lines in the first case are an unresolved doublet (as explained earlier) with the peak at the mean value of each doublet position the energy difference between the splittings for the two configurations of 0.4 meV will be given by $\Delta E = \mu_B |g| B$. Thus the hole g value is determined to be

$$g_h = -0.4 \pm 0.1 \ . \tag{1}$$

The sign of the hole g value is opposite to the sign of the spectroscopic initial-state g value, which has consistently to be derived in an electron-missing-electron picture.[17] It is clear that the initial state splitting of 0.20 meV is not sufficiently large to permit the observation of the doublet structure for $\vec{k} \| \vec{c}$, $\vec{B} \perp \vec{c}$. The anisotropic g value of the final electron state can be derived from Fig. 3 and 4 in conjunction with Fig. 5 to be

$$g_e^{\parallel} = -1.45 \pm 0.3, \quad g_e^{\perp} = -2.10 \pm 0.3. \tag{2}$$

Bearing in mind that in PbI_2 there is an inverted band structure as compared to III-V or II-VI compounds (there the conduction band is s like and the valence band is p like), one expects according to the pseudoacceptor model[18,19] which has been established for (A^0, X) complexes in direct gap III-V semiconductors the hole g value g_h of the initial bound exciton state to be equal to the valence band value g_v in PbI_2. Thus $g_v = -0.4$.

The sign of g_e agrees with a theoretical prediction made recently by Bimberg and Dean.[17] The electron in the present case has p-like character and has therefore to be compared with a hole in III-V or II-VI compounds. It was shown[17] that the bound hole g-value $\tilde{\kappa}$ is always negative because of band structure effects, in agreement with all experimental observations of these g values up to now.

One observation is unexpected on the basis of the above (D^0, X) model. The intensities of the two split Zeeman components should be in the ratio 1:1 for all magnetic field orientations, whereas experimentally a temperature independent ratio of ~3:1 between the low- and high-energy components is obtained. However, all other features are consistently explained and the parameters derived agree well with theoretical expectations.

For the case of an exciton bound to an ionized center, excluded in Sec. IV on the basis of the "two laser" experiment, similar difficulties with the relative intensities of the Zeeman split lines arise. For example, from Fig. 7(b) for the free exciton which for this configuration ($\vec{B} \| \vec{c} \| \vec{k}$) applies equally well to (D^+, X) or (A^+, X) it can be seen that a theoretical 1:1 intensity ratio of the split components, in the absence of thermalization, would again exist.

V. ANGULAR VARIATION OF ZEEMAN SPECTRA

Figure 6 shows the variation with angle between $\vec{B} \| \vec{c}$ and $\vec{B} \perp \vec{c}$ of the splitting of the bound exciton

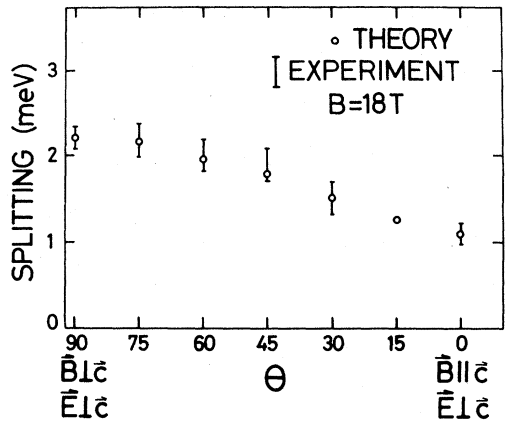

FIG. 6. Variation of the splitting of the bound exciton line with angle between $\vec{B} \parallel \vec{c}$ and $\vec{B} \perp \vec{c}$. The light was observed from the face of the crystal. θ is the angle between the magnetic field and the c axis of the crystal. The barred lines represent the experimental points and the circles the theoretical angular variation using the formula given in Eq. 6.

line at $B=18$ T. Using the previously determined g values and taking the electron g value to vary as $[(g_e^{\perp})^2 \sin^2\theta + (g_e^{\parallel})^2 \cos^2\theta]^{1/2}$ the circles given in the figure are obtained. To account for the unresolved doublet splitting the following fitting formula was used in order to allow for the increasing intensity of the π components with increasing θ:

$$\Delta E = \mu_B B\{[(g_e^{\perp})^2 \sin^2\theta + (g_e^{\parallel})^2 \cos^2\theta]^{1/2} - |g_h|(1-\sin\theta)\}. \quad (3)$$

The agreement between theory and experiment is seen to be quite good although the scatter and uncertainty in the experimental points does not permit a rigorous check of the g values already deduced from the $\theta = 0, 90°$ measurements to be made. The scatter in the points is probably caused by the random strains and stacking faults present in the crystal that will cause a perturbation of the energy of the exciton line varying as a function of position across the sample. Since it was impossible to keep the laser focused on the same point on the crystal surface during rotation some scatter in the rotation data was unavoidable.

VI. DIAMAGNETIC SHIFT OF THE BOUND EXCITON

A shift of the center of gravity of the Zeeman split bound exciton lines for $\vec{B} \perp \vec{c}$ of 0.2 ± 0.1 meV to higher energy was found at 18 T (see Sec. IV). Within the framework of a pseudoacceptor model[17-19] for (D^0, X) the center will behave as a free hole as far as diamagnetic effects are concerned. The final state of the transition is not expected to contribute to the observed shift. The condition for the applicability of this model is that the electron mass should be larger than the hole mass. By comparison with the situation in the III-V compounds and with that in zincblende and wurtzite II-VI compounds (e.g., CdS, CdSe) one would expect on general grounds that the mass of the p-like band was higher than that of the s-like band. On the other hand transport measurements by Minder *et al.*[20] indicate the reverse.

However, it is explained at the end of this section that even if m_h is greater than m_e, a similar interpretation of the diamagnetic shift can be made. The diamagnetic shift for (D^0, X) in the effective mass acceptor model is given by[17]

$$\Delta E_{\text{dia}} = \tfrac{1}{2}\gamma^2 R_h^* , \quad (4)$$

for $\gamma \ll 1$, where $\gamma = \hbar\omega_c/2R^*$, $\omega_c = eB/m_h c$, and R_h^* is the free-hole Rydberg. A hole mass of $0.195^{+0.05}_{-0.025}\, m_0$ and a hole Rydberg $R_h^* = 71^{+18}_{-9}$ meV can be deduced from $\Delta E_{\text{dia}} = 0.2 \pm 0.1$ meV, using $\epsilon_\infty = 6.1$.[21,22] The high-frequency dielectric constant was used in this calculation since $\omega_{\text{LO}} = 13.4$ meV in PbI_2.[21]

The hole mass calculated here can be used to derive an upper limit for the exciton binding energy E_x. Let us first assume that the electron mass is much larger than the hole mass. Then the isotropic excitonic Rydberg R_x^* will be approximately equal to (but somewhat smaller than) R_h^*. The correction to R_x^* due to the anisotropy of the electron mass will be negligible in this case since the electron mass does not contribute significantly to the Rydberg. Therefore $E_x \simeq R_x^* \leq 71^{+18}_{-9}$ meV. If, on the other hand, m_e is less than m_h, the pseudoacceptor model is not applicable here. The diamagnetic shift of the bound exciton would then be close to that of the free exciton. Consequently $R_x^* = 71$ meV assuming that an equation of the same form as (1) holds for an anisotropic system.[23] For mass values between these two limiting cases, similar conclusions can be drawn for E_x. This means that, independent of the actual mass ratio m_e/m_h, $E_x \leq 71$ meV, forcing a reinterpretation of the so-called "$n=3$" free exciton line. No diamagnetic shift of this line was observed in recent magnetoabsorption work within the experimental accuracy of 1 meV[3]. A much larger diamagnetic shift which varies as n^4 would be expected[3] for an $n=3$ exciton state on the basis of the present results since the value of $E_D = 0.2 \pm 0.1$ meV, which was found for the bound exciton represents a *lower* limit for the diamagnetic shift of the $n=1$ exciton state.

The situation regarding the $n=2$ state which

also was not observed to shift in the absorption measurements to within 1 meV is more difficult to assess. A shift of 3.2 ±1.6 meV for this state would be expected on the basis of the present measurements, using the perturbation theory approach of equation 4.[24] Alternatively the upper limit of ΔE of 1 meV from absorption implies $R_x^* > 105$ meV from Eq. (4). However, in view of the number of assumptions made in the analysis, for example the use of an isotropic hydrogenic model and the neglect of LO-phonon screening effects[22] and central cell corrections,[2] the apparent discrepancy between the two sets of results should not be regarded as evidence against the identification of the $n=2$ state.

VII. FREE EXCITON

No linear and quadratic Zeeman effects were observed in an investigation of the free exciton levels $n=1$, 2, and 3 in magnetic fields up to 18 T using absorption techniques.[3] However, the $n=1$ exciton line is always overabsorbed in such measurements even if crystals as thin as 1000 Å are used, and so its behavior in magnetic field could not be studied. In the present measurements several new effects have been found: (i) Without magnetic field the position of the $n=1$ exciton line is 0.8 meV lower for $\vec{k}\perp\vec{c}$ than for $\vec{k}\parallel\vec{c}$ (compare Figs. 2 and 4). (ii) With magnetic field a low-energy shift of 1 meV from 0 to 18 T of the exciton line for $\vec{k}\parallel\vec{c}\perp\vec{B}$ is found. For $\vec{k}\parallel\vec{c}\parallel\vec{B}$ the free exciton line is circularly polarized at 18 T [see Fig. 3(b)], the σ^+ component being shifted by 0.5 meV to lower energy compared to the zero-field position. The σ^- component is almost unobservably weak. Finally, for $\vec{k}\perp\vec{c}\parallel\vec{B}$ the exciton shifts by ~0.3 meV to lower energy from 0 to 18 T.

To explain these findings a group-theoretical discussion of the exciton states with and without magnetic field is given. The results are shown in Fig. 7(a)–7(e). The 1s exciton is composed of an A_4^+ hole and an A_4^- electron. The direct product gives three free exciton states:

$$A_4^+ \times A_4^- = A_1^- + A_2^- + A_3^- . \tag{5}$$

The wave vector $\vec{k}$ of the emitted light can be either oriented parallel or perpendicular to c. The subgroups for these two different orientations are the crystal space groups including the effect of the wave vector of the light, which has the effect of reducing the crystal symmetry from D_{3d} to D_3 for $\vec{k}\parallel\vec{c}$ and C_2 for $\vec{k}\perp\vec{c}$. An inspection of the selection rules for dipole transitions shows that the decay from the A_2^- state (in D_{3d}) is observable with $\vec{k}\perp\vec{c}$ and the decay from the A_3^- state (in D_{3d}) for $\vec{k}\parallel\vec{c}$. For $\vec{k}\perp\vec{c}$ A_3^- splits into two sublevels A_2+A_1 of which only A_2 can be observed (see Fig. 7); (in this figure the basis functions of the observable or partially observable levels are indicated using in each case the same coordinate system given at the bottom of the figure). The transition from the A_1^- state is always forbidden. The latter transition, which comes from the "singlet" exciton state is analogous to a $0\rightarrow 0$ transition in spherical symmetry. The shift of the exciton line to lower energy on going from $\vec{k}\parallel\vec{c}$ to $\vec{k}\perp\vec{c}$ [compare Figs. 2(a) and 4(a)] indicates that the A_2^- exciton state (in C_2) is shifted by ~ 0.8 meV to lower energy relative to the A_3^- exciton state, the

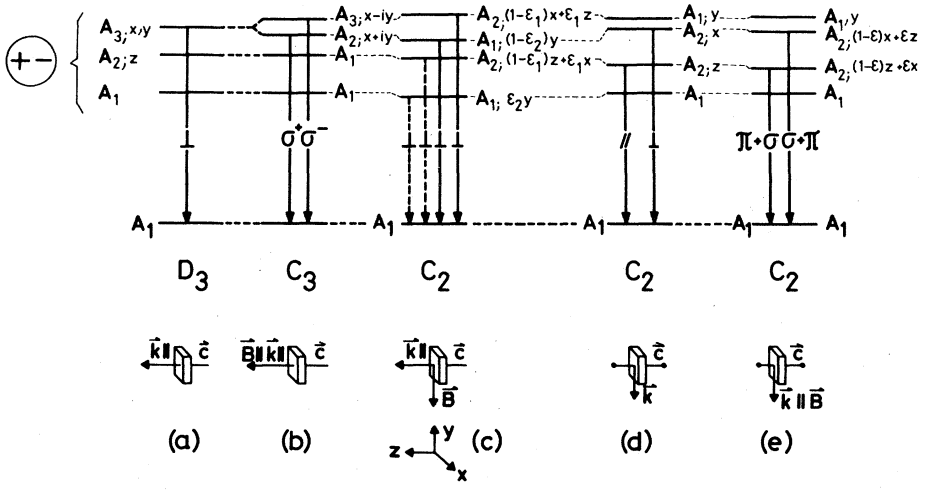

FIG. 7. Level scheme of the free exciton in PbI_2 (space group D_{3d}) for different orientations of the wave vector $\vec{k}$ of the light and of the magnetic field $\vec{B}$ relative to the c axis. $\perp$ and $\parallel$ mean polarized perpendicular or parallel to the c axis, whereas σ and π refer to the magnetic field axis. For some of the representations the basis functions are given in terms of the coordinate system shown at the bottom. ϵ means a magnetic-field-dependent matrix element close to zero. Allowed transitions are marked with straight lines; magnetic field induced transitions are marked with broken lines.

exact value depending on the degree of the thermalization (which is assumed to take place for the free exciton). This value agrees well with that of 0.6 meV reported by Pirozzi *et al.*[25] from an analysis of the long-range exchange splittings of the A_3^-, A_2^- excitons in PbI_2.

For a magnetic field $\vec{B}\|\vec{c}\|\vec{k}$ [Fig. 7(b)] the A_3^- exciton, which is composed of two oscillators polarized in the x-y plane, splits into $A_3^-(x-iy)$ and $A_2^-(x+iy)$ levels. σ^+ and σ^- transitions are allowed, the σ^+ being considerably stronger because of thermalization into the lower of the two split levels. From the shift of σ^+ to lower energy of 0.5 meV compared to the $B=0$ position the free exciton g value for $\vec{B}\|\vec{c}$ $g_{ex}^{\parallel}$ is found to be 1.0 ± 0.5 (the diamagnetic shift would act to increase this to 1.2). This value is in agreement within experimental error with that deduced by Vance *et al.*[26] of $g_{ex}^{\parallel}=1.5\pm0.5$ from magnetic circular dichroism measurements.

For $\vec{B}\perp\vec{c}\|\vec{k}$ [Fig. 7(c)] the situation is a little more complicated. Once again the $A_3^-(x,y)$ level splits into two levels with symmetries A_2^- and A_1^- in C_2. As indicated in Fig. 7(c) the $A_2^-(z)$ level unobservable for $\vec{k}\|\vec{c}$, is mixed by the magnetic field with the $A_2^-(x)$ level which is derived from the allowed A_3^- exciton (in D_{3d}) and so becomes weakly observable for the case of "small" magnetic fields. Similar arguments apply for the A_1 spin singlet state which is mixed with the $A_1(y)$ split sublevel of A_3 and so also becomes very weakly observable. However, the main effect on the experimental spectrum is the linear splitting of A_3 with the upper level once again becoming depopulated due to thermalization. From the observed shift of the free exciton peak of 1 meV to lower energy from 0 to 18 T, $g_{ex}^{\perp}$ is deduced to be $+2.0\pm0.5$. Having derived values for $g_{ex}^{\perp}$ and $g_{ex}^{\parallel}$ the anisotropic free-electron g value can be determined directly from

$$g_{ex}^{\perp,\parallel}=g_{e}^{\perp,\parallel}+g_h \tag{6}$$

Using the value of $g_h\simeq-0.4$ that was determined in Sec. VI, one obtains $g_e^{\parallel}=1.4\pm0.6$ and $g_e^{\perp}=2.4\pm0.6$.

For $\vec{k}\perp\vec{c}$ and a magnetic field $\vec{B}\|\vec{k}$ [Fig. 7(e)] no large change is expected from 0 to 18 T. Since the two A_2 levels have a repulsive interaction in a magnetic field, a small shift of the exciton recombination line to lower energy with increasing field is expected if thermalization occurs as has been assumed before. Indeed a shift of 0.3 meV to lower energy was observed at 18 T thus supporting the above assumptions regarding thermalization.

VIII. CONCLUSION

The first experimental investigation of the near band gap radiative recombination of $2H$-PbI_2 in magnetic fields up to 18 T is reported. An angular-dependent Zeeman effect of the dominating bound exciton line is observed. The binding center of the bound exciton is identified as being a neutral donor. The g values of the initial (D^0,X) state and of the final donor state are determined. The (D^0,X) g value ($g_h=-0.4$) can be identified with the free hole g value within the framework of a quasieffective mass acceptor model. A small diamagnetic shift of the BE line is observed at 18 T yielding a hole mass $m_h=0.195^{+0.05}_{-0.025}\,m_0$ and an effective mass acceptor binding energy of 71^{+18}_{-9} meV, which is at the same time an upper bound to the $n=1$ exciton binding energy.

The 1s free exciton shows an angular dependent shift to *lower* energy with magnetic field, yielding the angular-dependent exciton and free-electron g values. The size of the splitting of the two allowed zero-field states is estimated to be $\Delta E(A_3^- - A_2^-)\leq0.8$ meV.

Note added in proof. In very recent magnetoabsorption measurements on the $n=1$ free exciton line in PbI_2 N. Miura, G. Kido, and S. Chikazuma, in Proceedings of the Fourteenth International Conference on the Physics of Semiconductors, Edinburgh 1978, (unpublished) report a diamagnetic shift of 5 meV at 100 T. This corresponds to a diamagnetic shift of 0.2 meV at 20 T consistent with the acceptor diamagnetic shift of 0.2 ± 0.1 meV found in the present paper.

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