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Magnetoabsorption spectra of band-edge excitons in 2*H*-PbI_2 at high magnetic fields up to 40 T

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Magnetoabsorption spectra of band-edge exciton series in 2*H*-PbI_2 single crystals are measured up to 40 T with a configuration of $\mathbf{E}\perp\mathbf{c}\|\mathbf{B}$. This is a first observation of energy splittings and shifts of the three distinct exciton lines as a function of applied magnetic field. From the linear Zeeman splitting and diamagnetic shift of the ground-state absorption line, an effective g value is estimated as $g_\perp=0.89$ and the binding energy as 63 meV. The binding energy of the ground-state exciton is much smaller than the value in the model of Harbeke and Tosatti [J. Phys. Chem. Solids **37**, 126 (1976)].

There have been many works and interpretations about the nature of the exciton absorption lines (A_1, A_2, and A_3) which appear at the band edge in PbI_2. A typical example of the absorption spectra is shown in Fig. 1 for the sample used in the present experiment. The lines were first observed by Nikitine and Perny[1] who interpreted them as the $n=1$, 2, and 3 lines of a hydrogenic series with the Rydberg energy $\mathcal{R}$ (equivalent to the binding energy of the ground-state exciton E_B) of 142 meV which is deduced from the energy difference between the energy positions of the A_2 and A_3 lines. According to this interpretation the ground-state A_1 line should be anomalously displaced to the higher-energy side by 82 meV,[1] as is shown in Fig. 2 (model *a*). Harbeke and Tosatti proposed a model to quantitatively explain the energy shift of the ground state in terms of a repulsive central cell correction.[2] Gähwiller and Harbeke proposed $\mathcal{R}$ of 127 meV as for the 2*H* polytype.[3]

On the other hand, Baldini and Franchi suggested that the lines consist of two overlapping series both with $\mathcal{R}$ of 55 meV,[4] as shown in Fig. 2 (model *b*), by analogy of solid krypton spectra between 10 and 13 eV.[5] Le Chi Thanh *et al.* interpreted the lines as a normal hydrogenic series with $\mathcal{R}$ of 30 meV on the basis of an observation of a new line A_x in between the A_2 and A_3 lines, where they assigned the A_1, A_2, and A_x lines as the $n=1$, 2, and 3 states, respectively,[6] as shown in Fig. 2 (model *c*). Mussil *et al.* suggested that the A_2 line is the surface exciton by the study of Faraday rotation of PbI_2 thin films evaporated on NaCl substrates.[7] From the difference of electric-field effects between the A_1 and A_2 lines, Bordas *et al.* suggested that the A_2 line does not belong to the same exciton series as the A_1 line.[8]

As mentioned above, there is a large controversy as to the number and energy positions of the excitons in PbI_2. From magnetoabsorption measurements up to 18 T, Skolnick *et al.* reported that no measurable shift or splitting of the three lines could be observed within their experimental accuracy, and proposed a lower limit value of $\mathcal{R}=181$ meV, deduced from the A_3 line.[9] However, by a magnetoluminescence study of the bound exciton, they obtained the upper limit value of $\mathcal{R}=71$ meV,[10] which contradicts the previous result. On attempt to get further and more direct information, we have carried out precise magnetoabsorption measurements of these lines using strong pulsed magnetic fields up to 40 T.

The measurements were performed on very thin ($\sim$0.1 μm) samples of 2*H* polytype carefully cleaved from single

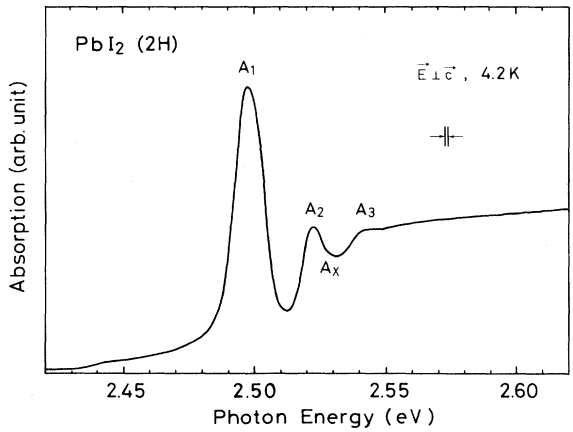

FIG. 1. Absorption spectra of 2*H*-PbI_2 with the configuration of $\mathbf{E}\perp\mathbf{c}$ at 4.2 K. Peak position of the absorption lines are compared with the previously reported data in Table I.

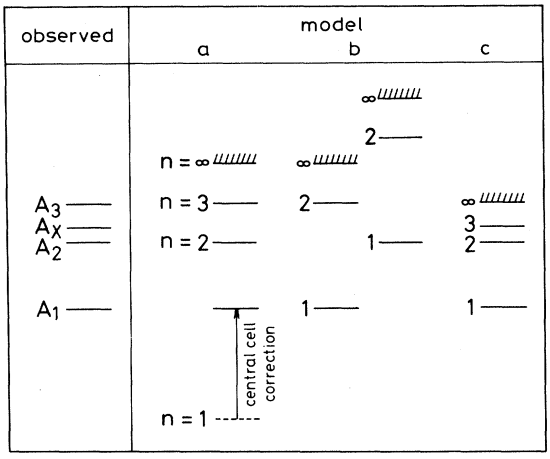

FIG. 2. Models for interpreting the band-edge exciton structure in PbI_2.

crystals grown by a traveling zone technique. These samples show three distinct absorption lines: A_1, A_2, and A_3. The A_x line appears as a shoulder at the high-energy side of A_2 line, as is shown in Fig. 1. The energy position of the three absorption lines are compared with previously reported data in Table I. Pulsed magnetic fields up to 40 T were generated by supplying a current from a 112-kJ capacitor bank into a coil which is made of superconducting wire cooled by liquid nitrogen. Magnetoabsorption spectra are measured by an optical multichannel analyzer (OMA) with a diode detector array installed at the exit of a spectrometer, opening the OMA gate at the top of a pulsed magnetic field.[12] The measurements are performed at a temperature of 4.2 K. Left or right circularly polarized light, $\sigma+$ or $\sigma-$ supplied by a pulsed tungsten lamp, is introduced onto a sample with a configuration of $\mathbf{E}\perp\mathbf{c}\|\mathbf{B}$, where $\mathbf{E}$ is an electric field of the incident light, $\mathbf{c}$ the crystal axis perpendicular to the layer of PbI_2 crystals, and $\mathbf{B}$ an applied magnetic field. The spectral resolution of the measurement is determined by an entrance slit width and it is normally 0.43 nm. The resolution for the energy shift of absorption lines is much better than this value. The variation of the magnetic fields during the measurements is less than 3% at the top of the pulsed magnetic field.

An example of the typical experimental recordings of the magnetoabsorption spectra is shown in Fig. 3. Each spectrum is measured at a magnetic field indicated on the right-hand side of the spectra, and at a temperature of 4.2 K with the configuration of $\mathbf{E}\perp\mathbf{c}\|\mathbf{B}$ for the $\sigma+$ polarization. Spectra for $\sigma-$ are also displayed for the highest magnetic field of 38.3 T by a dotted line for comparison. As is shown in Fig. 3, all the lines show shifts to the higher-energy side and give rise to splittings between the $\sigma+$ and $\sigma-$ polarizations with increasing magnetic fields. The lines with higher index numbers show a larger energy shift at high magnetic fields. However, the splittings are in the same order for all three lines. In addition, it is found that the absorption intensity of the A_2 line decreases, while that of the A_3 line increases with increasing magnetic fields.

The peak position of the A_1 line is shown in Fig. 4(a) as a function of magnetic field. The energy splitting and shift in a magnetic field are clearly observed. Figure 4(b) shows the energy differences between the two split components against the magnetic field. Figure 4(c) shows the energy shift of the middle of the two components against the square of magnetic field. The linear Zeeman splitting and the quadratic energy shift are evident in the figures.

TABLE I. Peak positions of the exciton lines in $2H$-PbI_2, in eV.

	A_1	A_2	A_x	A_3
Harbeke and Tosatti (Ref. 11)	2.496	2.520	· · ·	2.537
Le Chi Thanh *et al.* (Ref. 6)	2.499	2.521	2.527	2.538
Harbeke and Tosatti (Ref. 2)	2.497	2.519	· · ·	2.537
		2.524	2.529	2.542
Skolnick *et al.* (Ref. 9)	2.500	2.524	· · ·	2.542
Present work	2.496	2.521	2.528	2.541

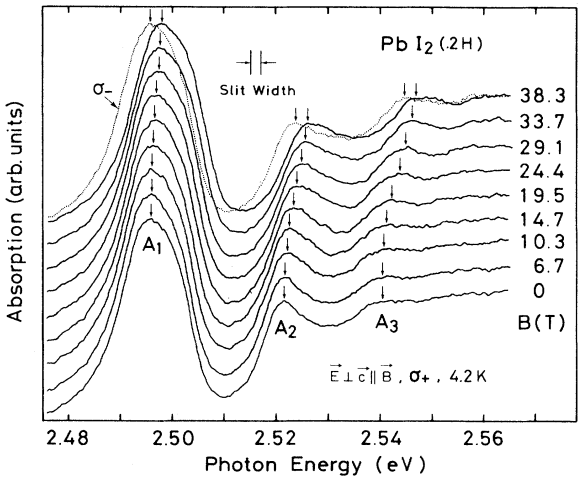

FIG. 3. Magnetoabsorption spectra of $2H$-PbI_2. The spectra were obtained at 4.2 K with the configuration of $\mathbf{E}\perp\mathbf{c}\|\mathbf{B}$ and $\sigma+$. Applied magnetic fields are indicated on the right-hand side to each spectrum. The spectra at 38.3 T, for the $\sigma-$ polarization are also shown by a dotted line.

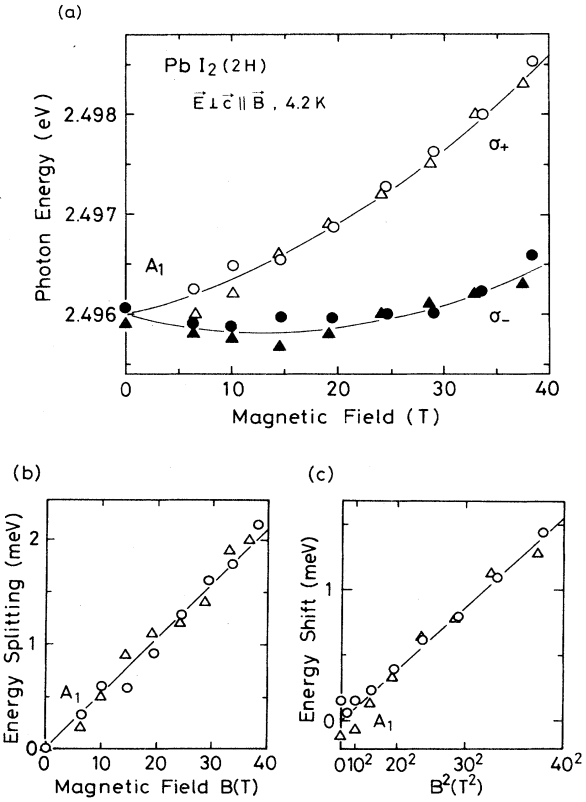

FIG. 4. (a) Energy position of the A_1 line as a function of magnetic field. Circles and triangles stand for different samples. The open and solid points represent the data for $\sigma+$ and $\sigma-$ polarization, respectively. (b) Energy splitting between peak position for $\sigma+$ and $\sigma-$ polarization as a function of magnetic field. (c) Energy shift against the square of magnetic field, where the energy shift is evaluated by averaging over two split lines of $\sigma+$ and $\sigma-$.

If the following hydrogenlike formula is applied to interpret the data in Fig. 4(a),

$$E = E_0 \pm \tfrac{1}{2} g_\perp \mu_B \mathbf{B} + c_0 \mathbf{B}^2 , \quad (1)$$

we obtain $g_\perp = 0.89 \pm 0.09$ and $c_0 = 9.7 \times 10^{-7}$ eV/T^2, where E_0 is the energy of the A_1 line at $\mathbf{B} = 0$, μ_B the Bohr magneton, $g_\perp$ defined as an effective g value perpendicular to the layer plane, and c_0 the coefficient of the diamagnetic shift.

Thus, the effective g value of the A_1 line obtained above is directly determined by the linear Zeeman splitting. It can be said that the previously determined value of 1.0 ± 0.5 by Skolnick *et al.* from a luminescence investigation[10] and that of 1.5 ± 0.5 by Vance *et al.* from the magnetic circular dichroism[13] are rather in good agreement with the present data. Figure 5(a) displays the energy splittings of the A_2 and A_3 lines against magnetic fields. We also obtain the effective g value of the two lines as $g_\perp = 1.22 \pm 0.12$ for A_2 and 1.14 ± 0.27 for A_3, respectively. Figure 5(b) shows the average of the two components of the A_2 and A_3 lines against the square of magnetic field. A dashed line in the figure is a calculated curve for the $n = 2$ state expected from the diamagnetic shift of the A_1 line ($n = 1$) based on a hydrogenlike exciton theory which is valid in the intermediate magnetic field range.[14] The A_2 line shows the $\mathbf{B}^2$ dependence only in low magnetic fields below 15 T as shown by a dot-dashed line. The value of c_0 for the A_2 line is estimated to be about five times as large as that of the A_1 line in the low magnetic field range. This energy shift of the A_2 line is significantly smaller than the calculated curve. This discrepancy is due to the exciton-phonon interaction as will be discussed later. The peak position of the A_3 line does not show an appreciable change below 18 T as reported by Skolnick *et al.*[9]

The value of c_0 for A_1 obtained in the present experiment is larger than previously reported data 5.4×10^{-7} eV/T^2 for evaporated thin films.[15] Evaporated thin films are normally polycrystalline, and integrated properties over many crystals with different orientations or with different polytypes are observed. Therefore, the value of c_0 in the present experiment with single crystals is considered to be an accurate value for $2H$-PbI_2 and $\mathbf{B} \| \mathbf{c}$. We have also investigated magnetoabsorption spectra with the configuration of $\mathbf{E} \perp \mathbf{c} \perp \mathbf{B}$. In this configuration, the exciton spectra exhibit complicated changes in high magnetic fields, but we obtained a value of c_0 roughly half of the present value.[16]

From the value of c_0 with the configuration of $\mathbf{E} \perp \mathbf{c} \| \mathbf{B}$, we can estimate reduced exciton mass $\mu_\perp$, binding energy E_B, and exciton Bohr radius a_0 of the ground-state exciton by use of the formula applicable to the case where the anisotropy is not too large:

$$c_0 = \frac{4\pi^2 \hbar^4 \epsilon_\perp \epsilon_\|}{\mu_\perp^3 e^2} , \quad (2)$$

$$E_B = \frac{\mu_\perp e^4}{32\pi^2 \hbar^2 \epsilon_\perp \epsilon_\|} , \quad (3)$$

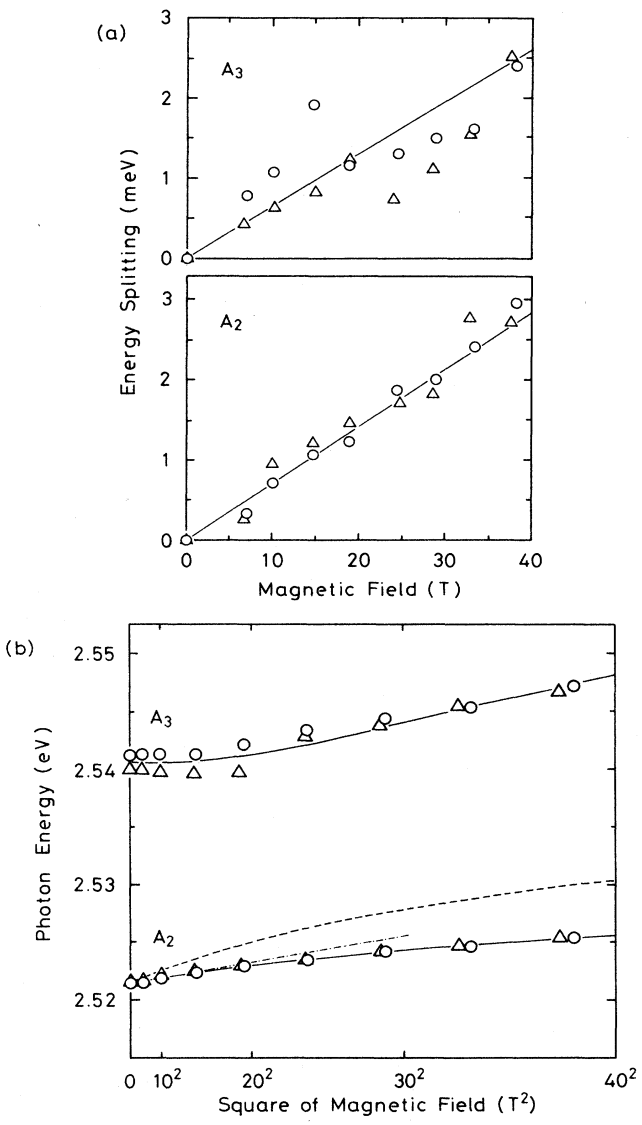

FIG. 5. (a) Energy splitting of the A_2 and A_3 lines against magnetic field. (b) Energy shift of the A_2 and A_3 lines against the square of magnetic field. The dashed line is a calculation curve for the $n = 2$ state expected from the diamagnetic shift of the A_1 line. The dot-dashed line is a guide to the eye showing the $\mathbf{B}^2$ dependence of the A_2 line in low-field range.

and

$$a_0 = \frac{4\pi \sqrt{\epsilon_\perp \epsilon_\|} \hbar^2}{\mu_\perp e^2} , \quad (4)$$

where e is charge of an electron and $\epsilon_\perp$ and $\epsilon_\|$ dielectric constants. Here, as for the dielectric constants, we employ the high-frequency one determined by an infrared reflectivity study: namely $\epsilon_{\infty\perp} = 6.1\epsilon_0$ and $\epsilon_{\infty\|} = 5.9\epsilon_0$, where ϵ_0 is a dielectric constant in a vacuum.[17] A use of this value is thought to be appropriate when one investigates the ground-state exciton of which binding energy is much larger than the LO-phonon energy 13.4 meV.[17] Thus we obtained $\mu_\perp = 0.17 m_0$, $E_B = 63$ meV, and $a_0 = 1.9$ nm, where m_0 is a free-electron mass.

The A_2 line is hardly considered to be a surface exciton, because the line is quite stable and repeatedly observed in every measurement for the same samples. This is in contrast to the case of the same layered material BiI_3, in which the surface exciton is very sensitive to the surface conditions and observed only when special surface treatments are made.[18]

If the A_2 line is the ground state of another exciton series with different binding energy from that of the A_1 line, the A_2 line should correspond to a very shallow level as is expected from the large diamagnetic shift. However, such a direct transition is not expected from the band calculation.[19] If the PbI_2 exciton structure consists of two overlapping series, each of which starts from the A_1 and A_2 lines, with the same binding energy as model *b*, they should exhibit the same diamagnetic shift. However, the observed energy shift of the A_2 line is about five times as large as that of the A_1 line. Therefore, such a model (model *b*) is denied by the present investigation as well as by the polarization dependence observed by Harbeke *et al.*[11]

Pollman *et al.* suggested that the exciton and LO-phonon interaction gives rise to a large polaron effect for excitons in PbI_2.[20] If we take account of the polaron effect in the interpretation of PbI_2 exciton structure, the true binding energy of the ground state should be larger than that determined from the energy difference between the observed exciton lines, because the polaron effect to the excited states is larger than that to the ground state.[21] Therefore, it is concluded that the binding energy determined from energy positions of the exciton absorption lines has to be smaller than 63 meV, which is estimated in the present magnetoabsorption measurement. Therefore, model *a* regarding the A_2 and A_3 lines as the $n=2$ and 3 states is also denied, because the binding energy 127 meV based on the model is much larger than 63 meV, contrary to the above idea.

A remaining interpretation is that of model *c*. If we examine model *c* in Fig. 2, the interval between A_2 ($n=2$) and A_x ($n=3$) requires that the binding energy E_B should be 30 meV, in the framework of the hydrogenlike model. This value of E_B is considerably smaller than 63 meV evaluated from the diamagnetic shift. However, the decrease of the energy levels by the polaron effect is larger for $n=2,3$ levels than the ground state. Therefore, this difference may be explained by the polaron effect. In fact, according to the variational calculation of the polaron effect,[16] the interval between the levels based on model *c* can be consistently explained with the amount of the observed diamagnetic shift. This model, in conjunction with the polaron effect, seems plausible as will be discussed in Ref. 16.

In view of model *c*, a question arises concerning the origin of the A_3 line. Without taking the exciton-phonon interaction into account, the binding energy of the A_2 line ($n=2$) is estimated as 16 meV. This value is slightly larger than the LO-phonon energy 13.4 meV. In such a situation, it is predicted by Toyozawa and Hermanson that the exciton is strongly coupled with the LO phonon and an exciton-phonon bound state is constructed and observed as an exciton-phonon sideband in the continuum region.[22] Therefore, it is expected that the A_3 line is attributed to the exciton-phonon bound state associated with the A_2 line ($n=2$) and the LO phonon. Based on the group theory, the first exciton-phonon sideband is forbidden but the second one is allowed. The energy position of the A_3 line is a little smaller than the energy of the A_2 line ($n=2$) plus 2LO-phonon energies. From these considerations, we propose the A_3 line may originate from the exciton-phonon bound state.

In conclusion, the band-edge exciton structure in $2H$-PbI_2 was studied by high-field magnetoabsorption measurements. Discernible energy shifts and splittings of the exciton lines are observed for the first time. The effective *g* values of three distinct exciton lines are determined from the linear Zeeman splittings, and they are found nearly the same. The binding energy of the ground state is estimated as 63 meV from the diamagnetic shift of the ground-state absorption line. By the present high-field magnetoabsorption experiment, it was revealed that the series of the exciton lines are explained in terms of model *c* by taking the polaron effect into account.

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