Magneto-optical effects observed for GaSe in megagauss magnetic fields

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Magnetoabsorption spectra of a layered compound GaSe have been measured both for the Faraday and for the Voigt configurations with magnetic fields up to 150 T. Interband transitions between the Landau subbands have been clearly observed for the Faraday configuration. The exciton exhibited a diamagnetic shift, from which we estimated the reduced mass of the exciton, $\mu_{\perp}=0.15$ and $\mu_{\parallel}=0.13$. The anisotropy of the reduced mass is surprisingly small in spite of the layered structure of the crystal. We have also observed the anticrossing effect between the $2s$ and the $3d_0$ states of the hydrogen-atom-like excitonic states. We discussed the correspondence between the excitonic states in a relatively low magnetic field and the Landau states in a high magnetic field.

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I. INTRODUCTION

Electronic and optical properties of GaSe have been extensively investigated from many points of view. In early days, the anisotropy of electronic states has been explored in connection with the layered structure of the crystal.[1] Recently, this material has attracted attention as suitable buffer layers for fabricating heterostructures in electronic devices,[2] and epitaxial growth by the molecular-beam epitaxy (MBE) has been attempted.[3–5] GaSe is a kind of standard materials for studying excitons and interband optical processes. Because the small oscillator strength of the exciton transitions enables us to measure transmission spectra of the crystal without too much difficulty, while in many other crystals it is difficult to obtain transmission spectra near the energy gap due to the large absorption coefficient. Magneto-optical measurement is a powerful tool to study fundamental properties of materials. Many papers have been published concerning magneto-optics of GaSe.[6–10]

A dimensionless parameter $\gamma \equiv (\hbar eB/2\mu^*)/R^*$ is often used to represent the relative strength of the magnetic field in materials, where B is the magnetic field, μ^* is the effective reduced mass of a electron and a hole, R^* is the effective Rydberg energy, and $\hbar eB/2\mu^*$ corresponds to the zero-point energy of the Landau levels. As γ becomes unity at ~ 50 T in GaSe, the magnetic field much larger than 50 T is necessary to investigate the magneto-optics in the strong magnetic-field regime. Many of the previous works have been done under the condition $\gamma \leqslant 1$.[7–9] Although some papers reported the results for $\gamma > 1$,[6,10] they provided spectra only for the Faraday configuration. In this work, magnetoabsorption spectra both for the Faraday and for the Voigt configurations were systematically measured in magnetic fields up to 150 T in order to discuss the fundamental properties of the exciton and the energy band in GaSe.

II. EXPERIMENTAL PROCEDURE

Thin films of GaSe were prepared by cleaving a single crystal. The typical thickness of the films is ~ 30 μm. The c axis of the crystal is perpendicular to the surface plane of the films. Magnetoabsorption spectra in pulsed magnetic fields have been measured by two different systems. One consists of a nondestructive solenoid coil, a spectrometer, and an optical multichannel analyzer system.[11] Spectra are measured during the flat part at the top of the pulsed magnetic fields. The pulse width is ~ 10 ms and the maximum field is ~ 50 T. Samples are immersed in liquid-helium bath. The other is a single-turn coil system. It is combined with a spectrometer, a streak camera, and a charge-coupled device (CCD) camera.[12] The pulse width is ~ 10 μs and the maximum field is ~ 150 T. Time-resolved spectra during the whole pulse duration are recorded continuously on the CCD as a two-dimensional image. Spectra at different magnetic fields are obtained from the image. Samples are cooled by flowing liquid helium near the sample. Although the maximum field is smaller in the former system, the S/N ratio and the homogeneity of the magnetic field are better than those in the latter system. Therefore, the former system is adopted to measure magnetoabsorption spectra in the relatively low magnetic-field range up to 40 T. While different films were prepared for the two kinds of measurements to fit each sample holder, all films are cleaved from the same single crystal. Magnetoabsorption spectra have been obtained both for the Faraday configuration with $B \| c$ and for the Voigt configuration with $B \perp c$. The electric field E of the incident light is perpendicular to the c axis in the both cases. Either left circularly polarized light σ_+ or right circularly polarized light σ_- is used in the measurement for the Faraday configuration. Linearly polarized light is used for the Voigt configuration, and the π and the σ polarizations correspond to $B \| E$ and $B \perp E$, respectively.

III. RESULTS AND DISCUSSIONS

Figures 1 and 2 show magnetoabsorption spectra at different magnetic fields for the σ_+ and the σ_- polarizations in the Faraday configuration. The spectra in Fig. 1 were measured by the nondestructive coil system, and those in Fig. 2

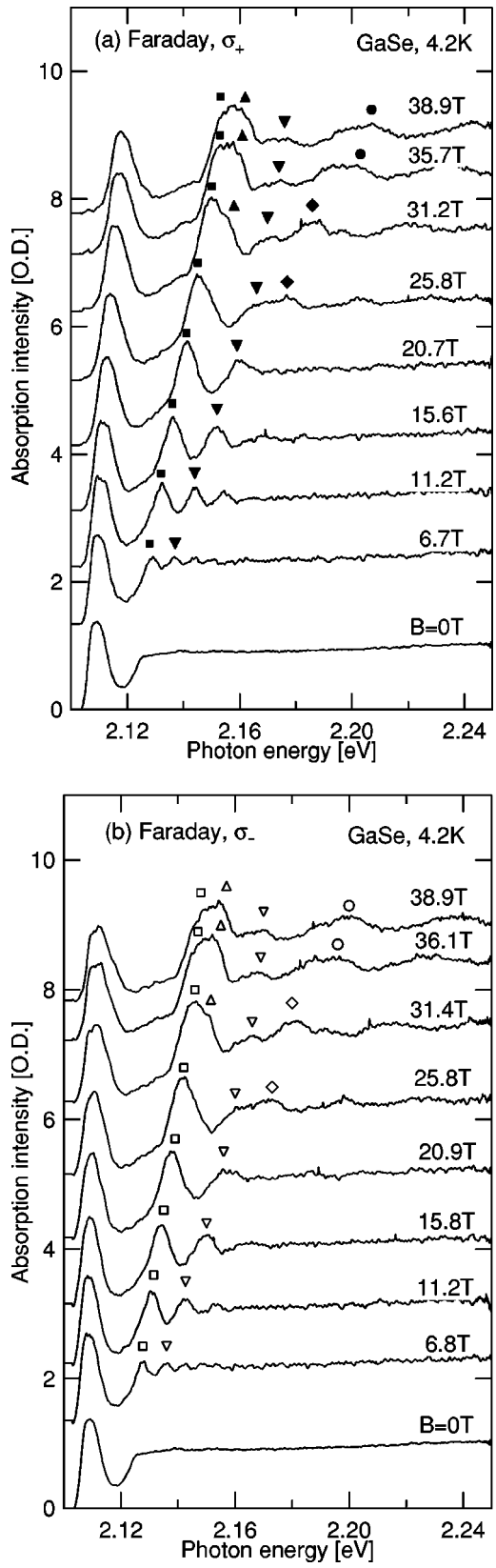

FIG. 1. Magnetoabsorption spectra at 4.2 K in different magnetic fields for the Faraday configuration; (a) for the σ_+ polarization, and (b) for the σ_- polarization.

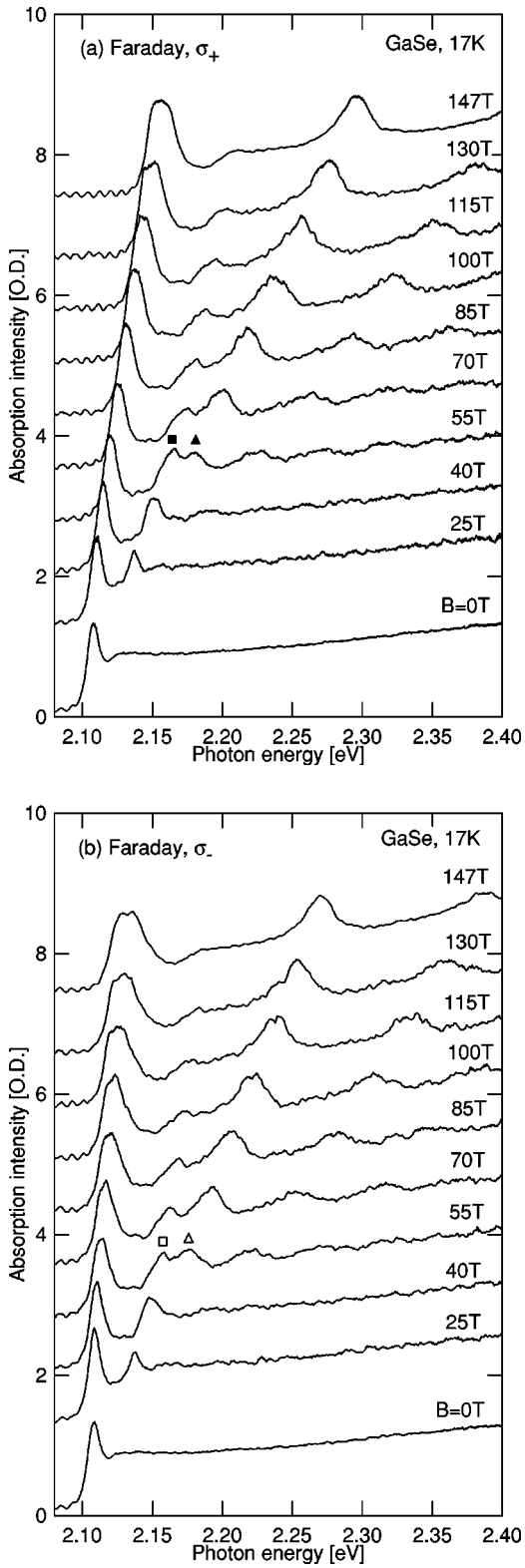

FIG. 2. Magnetoabsorption spectra at 17 K in different magnetic fields for the Faraday configuration; (a) for the σ_+ polarization, (b) for the σ_- polarization.

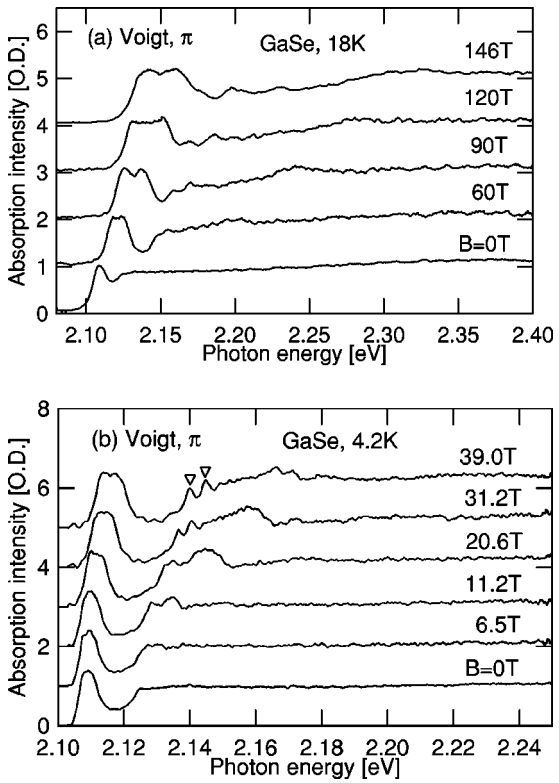

FIG. 3. Magnetoabsorption spectra in different magnetic fields for the π polarization of the Voigt configuration; (a) $B \leqslant 146$ T at 18 K and (b) $B \leqslant 39$ T at 4.2 K.

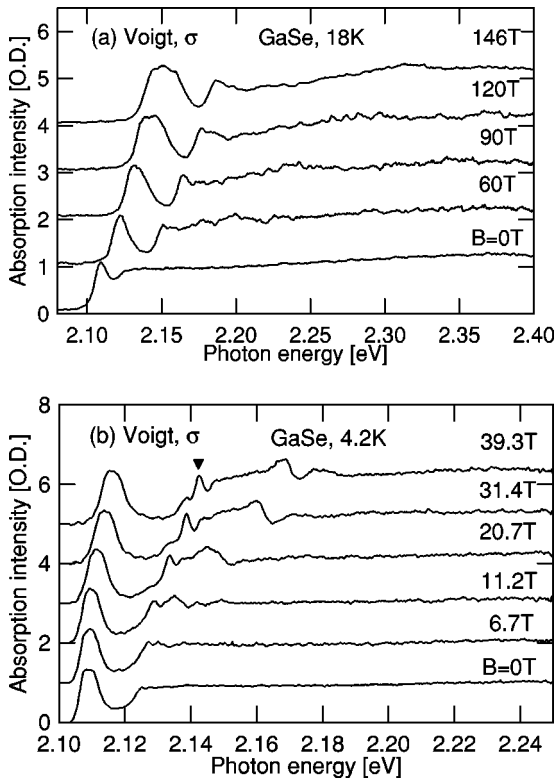

FIG. 4. Magnetoabsorption spectra in different magnetic fields for the σ polarization the Voigt configuration; (a) $B \leqslant 146$ T at 18K and (b) $B \leqslant 39$ T at 4.2 K.

by the single-turn coil system. In the spectra with $B=0$ T, the large absorption peak is the transition of a $1s$ exciton and a continuous absorption band lies above the exciton peak. The line shape of the $1s$ exciton peak at $B=0$ T in Fig. 1 is slightly different from that in Fig. 2, because different films were used in the two systems of measurement. The $1s$ exciton peak shifs to a higher energy with increasing magnetic field. Several peaks are observed under the magnetic fields, and they become prominent with increasing magnetic field.

Magnetoabsorption spectra for the π and σ polarizations in the Voigt configuration are shown in Figs. 3 and 4, respectively. The exciton peak splits into two components in strong magnetic fields for the π polarization, and the splitting energy of the exciton peak is almost proportional to the intensity of the magnetic field. The exciton peak for the σ polarization is located at the middle position of the two split lines for the π polarization in the same magnetic field.

The photon energies of the absorption peaks obtained from the spectra in Fig. 2 are plotted as a function of the magnetic field in Fig. 5. The photon energy of the $1s$ exciton peak for the σ_+ polarization is larger than that for the σ_- polarization in the same magnetic field. The energy difference of the exciton line between that for the σ_+ and that for the σ_- polarizations is proportional to the intensity of the magnetic field. The same energy difference is also observed for each peak above the exciton peak as seen in Fig. 5. Photon energies of the peaks represented by triangles in Fig. 5 are almost linearly dependent on the magnetic field. Their absorption intensities increase with increasing magnetic field. The peak represented by squares in Fig. 5 shows different behavior from other peaks. Its absorption intensity increases with increasing magnetic field up to ~ 50 T, while the peak is not so prominent in the strong magnetic fields.

Exciton states of GaSe have been theoretically examined by Schlüter.[13] The band-edge direct exciton state consists of Γ_4^s singlet state and $\Gamma_3^t+\Gamma_6^t$ triplet state. The singlet exciton transition is allowed for $E \| c$, while the triplet component Γ_6^t is weakly allowed for $E \perp c$ by the spin orbit interaction in the zero magnetic field. The exciton line observed in the present spectra corresponds to the above triplet exciton state. According to the theoretical model, the triplet exciton line consists of three degenerated states in the zero magnetic field, and it splits into three components in a magnetic field. Two of the three components can be observed for the Faraday configuration, and they are distinguished by a circularly polarized light. Indeed, the two lines were observed for the Faraday configuration and each of them appeared for the σ_+ or the σ_- polarization in the present experiment. In the above model, two of the three lines should appear for the π polarization of the Voigt configuration, while the other line should appear for the σ polarization at the central position of the two lines which appear for the π polarization. In the present spectra, actually the exciton line splits into two components for the π polarization of the Voigt configuration, and one line was observed for the σ polarization at the central position of the two components. The selection rule of the exciton line in the present magnetoabsorption spectra agrees well with the theoretical model.

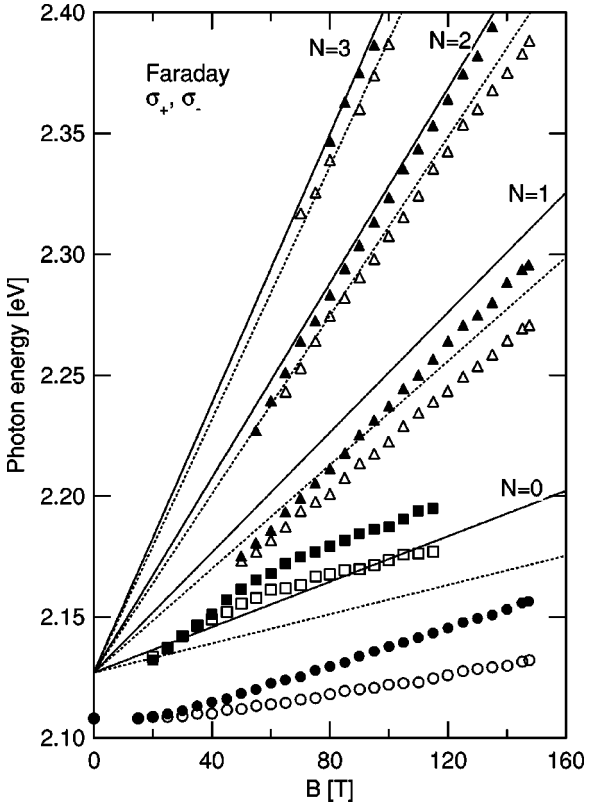

FIG. 5. Photon energies of the absorption peaks obtained from the magnetoabsorption spectra for the Faraday configuration. Solid markers (circles, squares, and triangles) correspond to the σ_+ polarization, and open markers to the σ_- polarization. Solid and broken lines are calculated for the σ_+ and the σ_- polarizations, respectively.

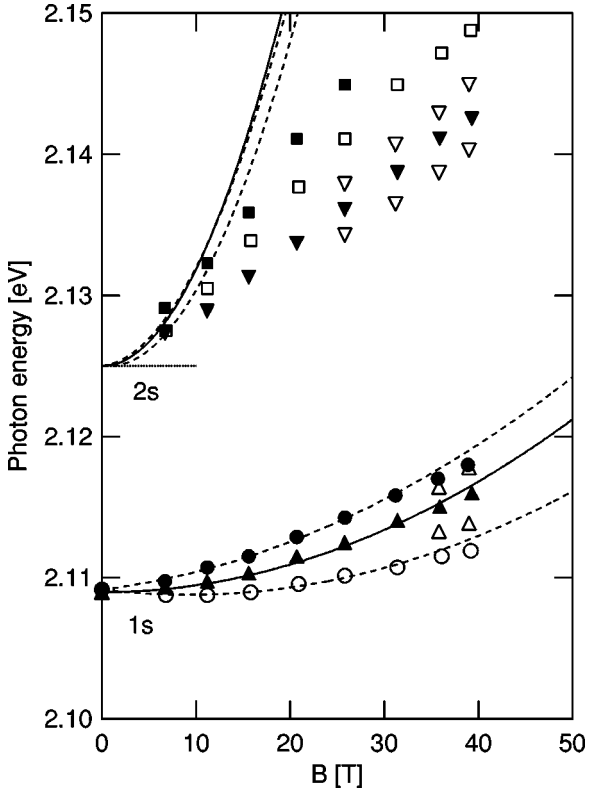

FIG. 6. Magnetic-field dependence for the photon energies of the absorption peaks. Those energies are obtained from the spectra in Figs. 1, 3(b), and 4(b). Solid circles and solid squares correspond to the σ_+ polarization of the Faraday configuration, open circles and open squares to the σ_- polarization, open triangles and open inverse triangles to the π polarization of the Voigt configuration, and solid triangles and solid inverse triangles to the σ polarization. Broken curves are calculated for the Faraday configuration, and solid curves for the Voigt configuration. Dotted line indicates the photon energy of the $2s$ exciton transition at zero field.

The effective g value for the exciton, which means the sum of g values for the electron and the hole, was estimated from the observed splitting of the exciton peak. We obtained $g_{\mathrm{eff}\parallel}=2.8$ and $g_{\mathrm{eff}\perp}=2.1$, where $g_{\mathrm{eff}\parallel}$ and $g_{\mathrm{eff}\perp}$ are the values when the magnetic field is parallel and perpendicular to the c axis, respectively. These values are in good agreement with the data determined by Mooser and Schlüter[14] ($g_{\mathrm{eff}\parallel}=2.7$ and $g_{\mathrm{eff}\perp}=1.9$).

The peaks induced by the magnetic field for the Faraday configuration are analyzed as the interband transitions between the Landau subbands. The photon energies of the peaks are fitted as a function of B;

$$E=E_g+\left(N+\frac{1}{2}\right)\frac{\hbar eB}{\mu_\perp}\pm\frac{1}{2}g_{\mathrm{eff}\parallel}\mu_{\mathrm{B}}B,$$

where E_g is the energy gap, $N=0,1,2,3,\ldots$ is the quantum number of the Landau levels, $\mu_\perp=1/[(1/m_{e\perp})+(1/m_{h\perp})]$ is the component perpendicular to the c axis of the reduced effective mass, $m_{e\perp}$ is that of the electron effective mass, and $m_{h\perp}$ is that of the hole effective mass. The last term corresponds to the Zeeman effect, and μ_{B} is Bohr magneton; $g_{\mathrm{eff}\parallel}=2.8$ is the same value obtained from the splitting of the exciton line mentioned above. $E_g=2.131$ eV is determined by the observed position of the exciton lines. The best-fit value of $\mu_\perp$ is $0.15m_0$. Fitted lines are shown in Fig. 5. According to the parameters given by Mooser and Schlüter[14] ($m_{e\perp}=0.17m_0$, $m_{h\perp}=0.8m_0$), $\mu_\perp$ becomes $0.14m_0$. This again agrees with the present experimental value. The peak for $N=0$ should not be observed in the present spectra because the $1s$ exciton peak is dominant in the present magnetic-field range.

The photon energy of the $1s$ exciton peak obtained from the spectra in Figs. 1, 1(b), and 1(b) is plotted versus B in Fig. 6. The exciton line exhibits the Zeeman splitting for the Faraday configuration. The central position of photon energies for the σ_+ and σ_- polarizations shifts to a higher energy with increasing magnetic field. The value of the energy shift is proportional to B^2 below $\sim$30 T. This quadratic dependence corresponds to the diamagnetic shift of the $1s$ exciton. The experimental values of the energy shift are fitted by an equation for the Faraday configuration,

$$\Delta E_{1\mathrm{s}}=\pm\frac{1}{2}g_{\mathrm{eff}\parallel}\mu_{\mathrm{B}}B+\sigma_\parallel B^2,$$

where $\sigma_\parallel$ corresponds to the coefficient of the diamagnetic shift when the magnetic field is applied along the c axis.

Fitted curves are shown in Fig. 6. $g_{\mathrm{eff}\|}$ is already fixed, and $\sigma_{\|}$ becomes 4.4×10^{-6} eV/B^2. As the exciton line does not exhibit Zeeman splitting for the σ polarization of the Voigt configuration, the magnetic-energy shift of the exciton line is dominated by the diamagnetic shift. We obtained $\sigma_{\perp}=4.9\times10^{-6}$ eV/B^2 for the Voigt configuration, where $\sigma_{\perp}$ is the coefficient of the diamagnetic shift when the magnetic field is applied perpendicular to the c axis.

The following equations are employed to discuss the coefficient of the diamagnetic shift for the $1s$ exciton in an anisotropic system.[15]

$$\sigma_{\|}=\sigma\frac{\mu^2}{\mu_{\perp}^2},\quad \sigma_{\perp}=\sigma\frac{\mu^2}{\mu_{\perp}\mu_{\|}},\quad \sigma=\frac{\hbar^4\varepsilon^2}{32\pi\mu^3e^4},$$

$$\varepsilon=(\varepsilon_{\perp}^2\varepsilon_{\|})^{\frac{1}{3}},\quad \frac{1}{\mu}=\frac{\varepsilon}{3}\left(\frac{2}{\varepsilon_{\perp}\mu_{\perp}}+\frac{1}{\varepsilon_{\|}\mu_{\|}}\right),$$

where $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ are the components of the dielectric constant tensor parallel and perpendicular to the c axis, respectively. $\mu_{\|}/\mu_{\perp}=\sigma_{\|}/\sigma_{\perp}=0.9$ is obtained from the experimental values. Using the constants of Mooser and Schlüter,[14] $\sigma_{\|}$ and $\sigma_{\perp}$ should become 4.0×10^{-6} eV/B^2 and 4.7×10^{-6} eV/B^2, respectively. Those values are in good agreement with the present experimental ones.

The $2s$ exciton peak has been detected in the spectrum of a relatively thick sample prepared from the same single crystal. The photon energy of the $2s$ exciton in the zero magnetic field is indicated by a horizontal dotted line in Fig. 6. A small absorption peak appears above the $1s$ exciton peak in the magnetic field for the σ polarization of the Voigt configuration, which is indicated by inverse triangles in Figs. 3(b) and 4(b). A splitting of the line is observed for the π polarization as well as for the $1s$ exciton peak. Photon energies of the peaks are indicated by inverse triangles in Fig. 6. We assigned this peak as the 2s exciton. In the Faraday configuration, a peak indicated by squares in Figs. 1 and 2 is assigned to the $2s$ exciton line. The coefficient of the diamagnetic shift for the $2s$ exciton is theoretically 14 times as that for the $1s$ exciton. The curves for the $2s$ exciton are drawn by using $14\sigma_{\perp}$ and $14\sigma_{\|}$ in Fig. 6. The observed positions of the $2s$ line are almost on the curves at $B\sim7$ T, but they are significantly lower than the curves in high fields.

Several small peaks including the $2s$ exciton line are observed around the energy gap in the magnetic field below $B\sim10$ T for the Faraday configuration as seen in Fig. 1. Similar spectra were obtained by Rasulov *et al.*[8] and Halpern.[9] They observed some absorption lines having oscillatory structure for the Faraday configuration with the magnetic fields up to 10 T. These peaks look like the transitions between the Landau subbands, however, the magnetic field is too low to reach the high magnetic regime. In the following, we discuss the correspondence between the observed peaks in the low magnetic field ~10 T and in the high magnetic field over 100 T.

Shinada *et al.*[16] proposed a scheme of correspondence between the energy levels of a hydrogen-atom-like state in the low-magnetic-field regime ($\gamma\ll1$) and those in the high-magnetic-field regime ($\gamma\gg1$) and discussed magnetoabsorption spectra of GaSe up to 10 T. Considering the scheme given by Shinada *et al.*, we assign the peak indicated by squares in Fig. 1 as the $2s$ state, the peak indicated by triangles as the $3d_0$, the peak indicated by reverse triangles as the $3s$, and the peak indicated by rhombi as the $4d_0$. While the $3d_0$ and the $4d_0$ transitions are optically forbidden at the zero magnetic field, they becomes gradually allowed ones due to the mixing with the s-like states in a magnetic field. The $3d_0$ line appears at $B\sim30$ T in the spectra, and its absorption intensity increases with increasing magnetic field. The line tends to the observed peak indicated by triangles in Fig. 2, which has been assigned to the transition of the $N=1$ Landau subband. The $2s$ line, which is indicated by squares in Fig. 2, becomes weak in high magnetic fields. The energy difference between the $2s$ and $3d_0$ lines increases rapidly with increasing magnetic field. This is due to an anticrossing of the two states. The deviation of the $2s$ exciton line from a simple B^2 dependence as shown in Fig. 6 is probably caused by this anticrossing effect. The $3s$ line shows a behavior similar to the $2s$ line, which becomes weak over $B\sim25$ T and is repelled by the $4d_0$ line. The peak indicated by circles is possibly a $5g_0$ state, because it appears above the $4d_0$ and continues to the $N=2$ line of the Landau subbands.

In conclusion, magnetoabsorption spectra of GaSe thin crystals have been measured both for the Faraday and for the Voigt configurations with the magnetic fields up to 150 T. The interband transitions between the Landau subbands are clearly observed in the magnetic field over ~50 T for the Faraday configuration. $\mu_{\perp}$ is obtained to be 0.15 from the analysis. $\mu_{\|}$ is estimated to be 0.13 from the observed diamagnetic shift, which is smaller than $\mu_{\perp}$. The anisotropy of the reduced mass is small ($\mu_{\|}/\mu_{\perp}\sim0.9$). We clarified experimentally the joining relation between the hydrogen-atom-like excitonic states in relatively low magnetic fields and the Landau-level-like states in high magnetic fields. The small peaks in the magnetic fields up to ~10 T, which have been observed also by Rasulov *et al.*[8] and of Halpern,[9] do not directly continue to the transitions of the Landau subbands.

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