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V-2. Magneto-Optical Studies of Exciton Effects in Layer-Type Semiconductors

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Both experimental and theoretical works were performed with particular reference to a layer-type semiconductor, GaSe, for a coherent treatment of the exciton-like and the oscillatory Landau-like spectra appearing in a form of their combination in semiconductors in magnetic fields. The interband magneto-absorption and the Faraday rotation were measured in pulsed magnetic fields up to ~200 kOe at low temperatures. The theoretical analysis was based mainly on the exact solution for an extremely anisotropic semiconductor in the magnetic field of arbitrary intensity. The exciton effects are discussed in terms of the energy spectrum, the spectral intensity, and the spectral width by the use of the band parameters reduced from the experimental results.

§ 1. Introduction

Recent observation[1,2] of the oscillatory magneto-absorption accompanied by the well-resolved exciton lines in various semiconductors in a magnetic field has necessitated the physical understanding of the nature of the exciton in a wide range of the magnetic field. The problem of the exciton in a magnetic field has been solved in the limiting cases of the field either very high[3] (quasi-Landau level) or very low (Zeeman splitting with diamagnetic shift) relative to the field which gives the cyclotron energy comparable to the exciton binding energy. The interrelationship between these two sets of solutions, however, has not seemed to be well understood. This is mainly due to the lack of the experimental results in a relatively high magnetic field and to the mathematical difficulty of solving the problem for the magnetic field of intermediate strength.

The purpose of this paper is to achieve a coherent treatment of the two types of spectra, *i.e.* the exciton and the oscillatory magneto-absorption spectra, which have been observed in a form of their combination in many cases of the magneto-optical measurements in a high magnetic field. For this purpose both experimental and theoretical works have been performed with particular attention to a layer-type semiconductor, GaSe. It will be shown how the diamagnetic shift of the exciton level quadratic to a magnetic field changes into the linear shift of a quasi-Landau level with the increase of the magnetic field. The exciton effects will be discussed also in terms of the spectral intensity and the width observed both in interband magneto-absorption and in the Faraday rotation experiments.

GaSe is suitable for our purpose by the various reasons: In the visible wave length region, it exhibits a well-resolved first exciton peak followed by a weak absorption continuum whose shape is like a step-function[4]. Thus the oscillatory magneto-absorption and the Faraday rotation may be observed easily in the above region of the wavelength. The transition for these spectra is direct-allowed, and its theoretical analysis is relatively simple. The exciton binding energy is of the order of 100 cm^{-1} (0.01 eV) which is comparable to the cyclotron energy of an electron-hole pair with the reduced mass of the order of 0.1 m in our maximum field of 200 kOe. Our theory to be compared with the experimental results is mainly based on the exact solution for the exciton problem in an extremely anisotropic semiconductors, so that it

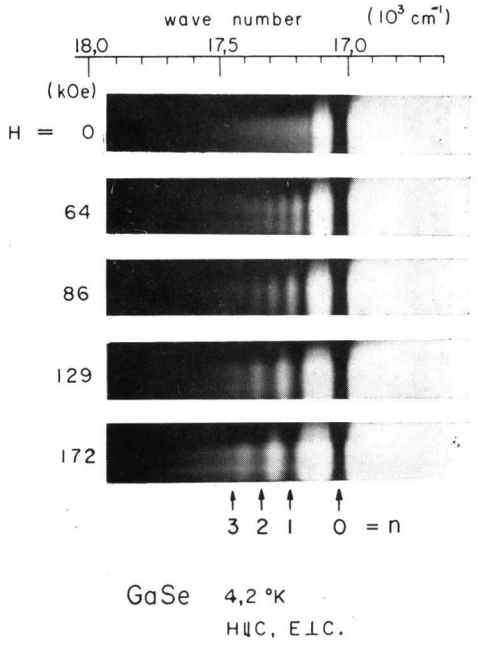

Fig. 1. Photographic print of the absorption spectrum of GaSe in the Faraday geometry at 4.2°K.

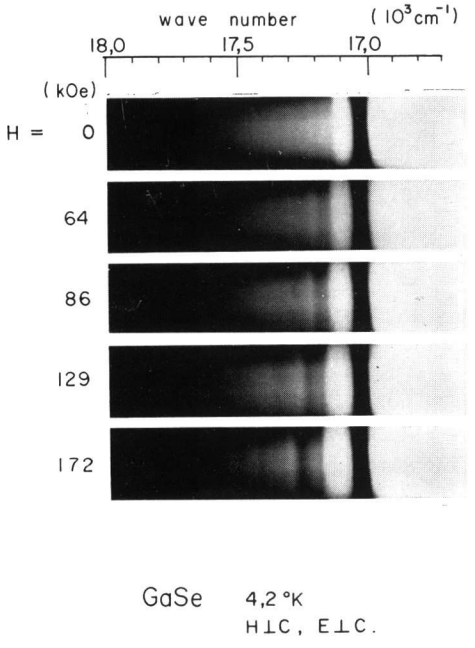

Fig. 2. Photographic print of the absorption spectrum of GaSe in the Voigt geometry at 4.2°K.

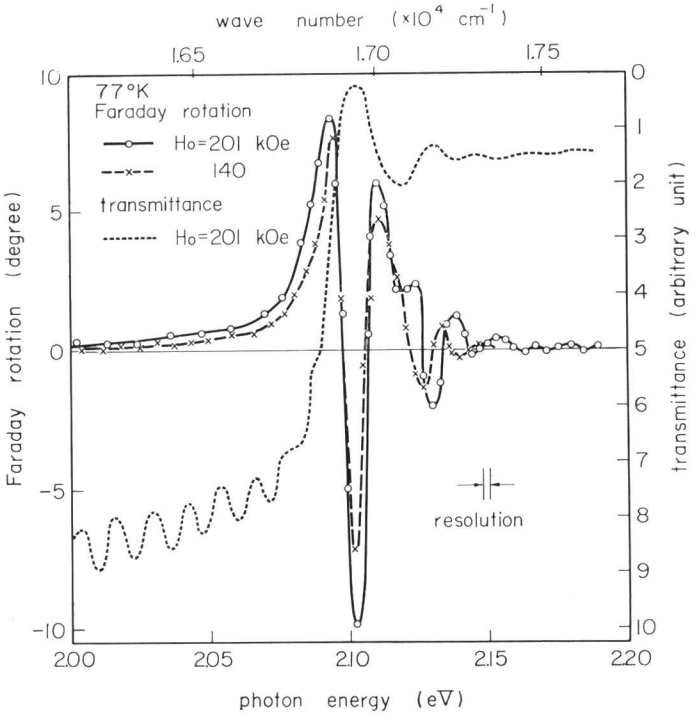

Fig. 3. The Faraday rotation and the magneto-absorption of GaSe in the fields of 140 and 201 kOe at 77°K. The sample thickness is 15.4 μ.

is convenient, but not necessarily essential for our purpose, to use a sample with large anisotropy.

§ 2. Experimental

A. Oscillatory magneto-optical absorption in GaSe:

The absorption spectra were taken with the photographic method described previously[2,5] in the pulsed magnetic field at temperatures 77, 4.2 and 1.7°K. The spectra did not show any remarkable dependence on the temperature. The magnetic fields were up to 180 kOe. The light was incident always parallel to the anisotropy axis C of the crystal. The photographic prints of the spectra at 4.2°K both in the Faraday and the Voigt geometries are shown in Figs. 1 and 2, respectively.

In the Faraday geometry, four or five oscillatory peaks are seen besides the first exciton peak. The amplitude of the oscillation decreases as one goes to higher peaks, and finally the oscillation disappears in the background continuum of the oscillation. The spectral width of the oscillation peak increases with the increase of the magnetic field.

B. Interband Faraday rotation in GaSe:

Simultaneous measurements of the interband magneto-optical absorption and the Faraday rotation were performed by a photo-electric method[6] in pulsed magnetic fields up to 201 kOe at liquid nitrogen temperature.

A typical example of the measured dispersion curves of the Faraday rotation in the fields of 201 and 140 kOe are shown in Fig. 3. The energies of the three minima in the dispersion curves at 16,950 cm^{-1} (2.102 eV), 17,180 cm^{-1} (2.130 eV), and 17,287 cm^{-1} (2.145 eV) for 201 kOe, are in good agreement with those for the oscillatory peaks in the magneto-absorption. The line shape of each oscillation in the dispersion curve is nearly symmetrical with respect to the photon energy for each minimum although the magnitude of the oscillation at higher energy wing is diminished considerably.

The magneto-absorption measured by the photo-electric method agrees with that measured by the photographic method.

§ 3. Energy Spectrum

The energies of the absorption peaks in the Faraday geometry are plotted against the magnetic field in Fig. 4. This may be obtained also from the dispersion of the Faraday rotation. It is seen in the figure that the energy of the first exciton peak, $n=0$, is almost independent of the magnetic field, while the energies of the oscillatory peaks, $n=1$, 2, 3, 4 and 5, in the absorption continuum shift almost linearly with the increase of the magnetic field if the field is higher than 40 kOe.

In Fig. 4 the corresponding theoretical curves for direct-allowed transitions are indicated. This curve was obtained by using the effective-mass theory: the solution of the effective-mass equation was obtained by solving at first the equation for an extremely anisotropic crystal where the reduced mass of the exciton parallel to the anisotropy axis $\mu_{\parallel}$ was infinite, and then by applying the corrections in accordance with the departure from $\mu_{\perp}/\mu_{\parallel}=0$, where $\mu_{\perp}$ was the reduced mass perpendicular to the anisotropy axis. The almost exact solution for an extremely anisotropic crystal was obtained by using both the methods of the WKB approximation[7] and the numerical integration[8] of the effective-mass equation.

The values of the parameters appearing in the effective-mass theory are determined so as to

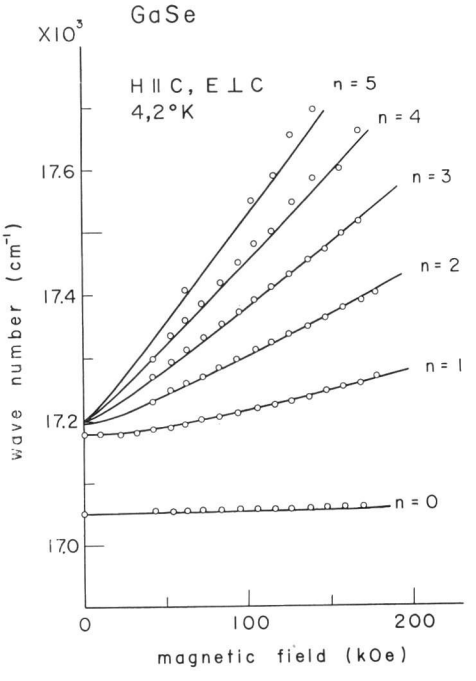

Fig. 4. Energies of the absorption peaks against the magnetic field H in the Faraday geometry at 4.2°K. Full lines represent the theoretical energy vs. H curves, in which the parameter values listed in Table I are assumed.

obtain the best fit of the theoretical curves to the experimental points. They are listed in Table I.

Table I. Values of the band parameters of GaSe.*

$\mu_\perp$	Energy gap	g	Effective Rydberg const.
0.138 m	17,204cm^{-1} (2.132$_9$eV)	3.3±0.1	76.5 cm^{-1} (9.48 meV)

* $(\mu_\perp/\mu_{//})^{1/3}=0.4$ is assumed to obtain the best overall fit.

In Fig. 4 we can see clearly the continuous change of the quadratic shift of the exciton levels into the linear shift of the quasi-Landau levels with the increase of the magnetic field. The exciton with $n=0$ does not seem to feel the magnetic field in our range of the fields, but its energy can be predicted to cross the $E=0$ line in the field of ~2 MOe[8]! In higher field region the energy level goes up almost parallel to the $n=0$ Landau level.

§ 4. Intensities

As mentioned in the previous section the amplitude of the absorption oscillation decreases as one goes up to higher peaks. The intensity of each absorption peak, the amplitude multiplied by the spectral width, is plotted against the peak number n in Fig. 5 and against the magnetic field in Fig. 6.

According to the effective-mass theory, the intensities of both the absorption and the Faraday rotation for the direct-allowed transitions are proportional to the squared amplitude of the envelope-function at the origin. Therefore, they are proportional to $(n+1/2)^{-3}$ ($n=0, 1, 2, \ldots$) for the exciton in an extremely anisotropic crystal ($n^{-3}(n=1, 2, \ldots)$ in an isotropic crystal) if no magnetic field is present. On the other hand they are independent of n and proportion-

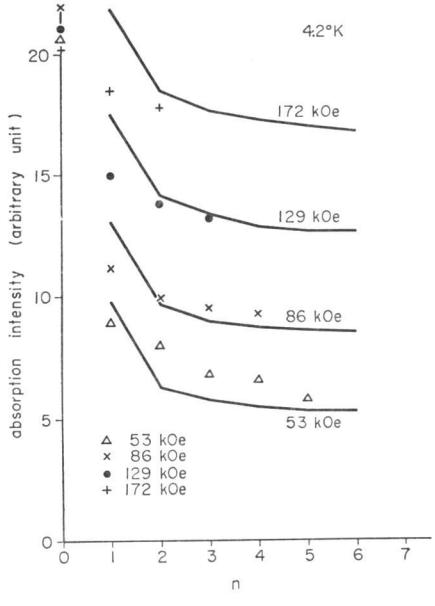

Fig. 5. Spectral intensities vs. the peak number n. The calculated points of the intensities for the extremely anisotropic case with the band parameters given in Table I are connected by full lines.

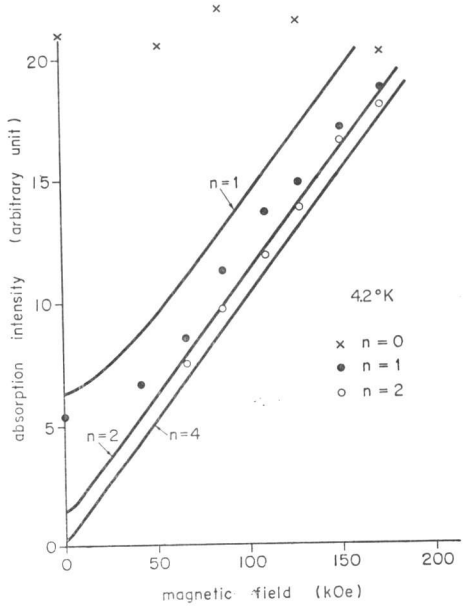

Fig. 6. Spectral intensities vs. magnetic fields. Full lines represent the theoretical intensities.

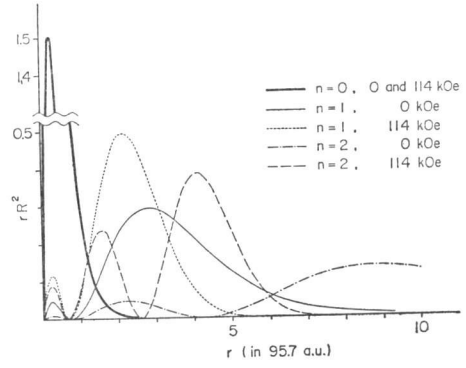

Fig. 7. Densities of the envelope-functions, rR^2 (r), with and without a magnetic field. r is given in the unit of the effective Bohr radius, 95,7 a.u.. The cyclotron radius at 114 kOe is 1.4×95.7 a.u..

al to the magnetic field if no exciton effect is taken into account. Our experimental results in the presence of the magnetic field in Figs. 5 and 6 apparently show none of these behaviours.

In the presence of a high magnetic field the envelope-function for the exciton is squeezed because of the diamagnetic term, resulting in the increase of the amplitude at the origin. This situation is clearly seen in Fig. 7 which shows the densities of the theoretical envelope-functions,[8] $rR^2(r)$, with and without a magnetic field. The function of $n=0$ is exceptional: it is not influenced at all in our range of the magnetic field. The effect of the squeezing increases with the increase of quantum number n. This characteristic is consistent with the experimental result that the intensity in the magnetic field approaches a nonvanishing value as n increases.

For qualitative camparison the calculated intensities for extremely anisotropic crystals are shown in Figs. 5 and 6 together with the experimental points. In our theory[7] the intensities are almost proportional to dE/dn, where E is the energy for the n-th level.

§ 5. Spectral Width

The line shape analysis of the dispersion curve of the Faraday rotation was made for a particular sample in the magnetic field up to 201 kOe. This gave the phenomenological g factors of $g=3.3\pm0.1$ and 3.4 ± 0.1 for the singularities at 16,950 cm^{-1}(2.102 eV) and 17,180 cm^{-1}(2.130 eV), respectively.

In the absorption experiment, no g-splitting was observed and the widths of the oscillatory peaks ($n\geq1$) were found to increase with the increase of the magnetic field, while for the $n=0$ peak no appreciable broadening was observed. The broadening of the oscillatory peaks can not be ascribed to the g-splitting only: if the spectral widths of the split components were field-independent and just those found in low fields in the oscillatory peaks, the g-splitting should be observed in high fields. This circumstance is explained in Fig. 8, where the modulation widths in the oscillatory absorption are plotted against the field together with the g-splitting derived from the Faraday experiment. It should be noted that the spectral width is broader than the modulation width and may be accounted for the phenomenological relaxation time, $\tau=(1.8\pm0.1)\times10^{-13}$ sec, found in the Faraday experiment.

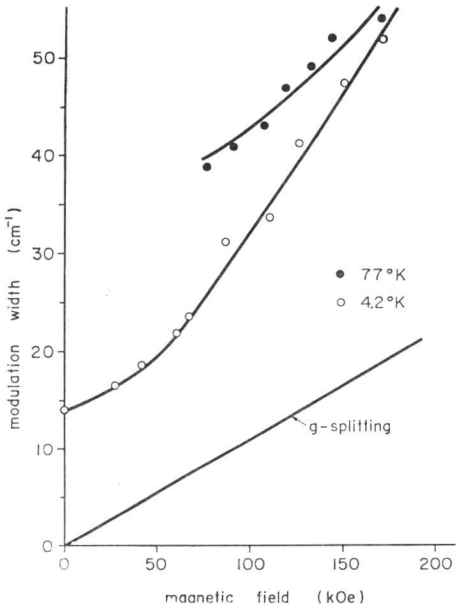

Fig. 8. Modulation widths in the oscillatory absorption vs. magnetic fields. For comparison the g-splitting derived from the Faraday experiment is indicated.

It may be concluded from our experimental results that the spectral width of each g-split component for a given oscillatory peak increases with the increase of the magnetic field, except for $n=0$ in which the width is rather field-independent.

One may consider the mechanism of the broadening as due to a kind of inhomogeneous effect: with the increase of the magnetic field the mass of the exciton band increases and finally in the high field range, where the picture of the quasi-Landau levels is valid, each quasi-Landau level is nearly degenerate with respect to different centres of the cyclotron motion. This degeneracy may be responsible for the inhomogeneous effect. The detailed mechanism of the inhomogeneous broadening dependent upon the magnetic field is now being studied in the light of the exciton effect.

Acknowledgements

The GaSe crystals used in our experiments were grown in the Cyanamid European Research Institute and we would like to express our sincere thanks to Dr. E. Mooser for providing us excellent GaSe crystals. This work was done

as one of the cooperative research projects in the Institute for Solid State Physics, Tokyo University.

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DISCUSSION

Mitchell, D. L.: The regularity of the experimental spectra and your method of analysis for the g-factor splitting seem to imply that both the valence and conduction bands are nondegenerate, apart from spin. Is this consistent with the theoretical band calculations of Kamimura and Nakao?

Kamimura, H.: Dr. Sugano's analysis is consistent with our analysis of the band structure. According to our analysis, the conduction band is orbitally degenerate. However, if we include the spin-orbit interaction, the orbital degeneracy is lifted, where the splitting is about 0.4 eV. Thus the conduction and valence bands have only the Kramers degeneracy, as Dr. Sugano assumed in his analysis.

Mooser, E.: In view of recent experimental results obtained by J. Halpern (absorption) and ourselves (emission) I should like to warn against the interpretation of the experimental line widths which are reported in the literature. It has been found that the early results on the zero-field line width were misleading because of inhomogeneous broadening and because of a splitting of the line into as many as 10 narrow lines. The inhomogeneous broadening is due to strain and the splitting can be interpreted in terms of the presence of different polytypes of GaSe. Unstrained crystals of one polytype only have been grown recently at our lab. They have linewidths 5 times narrower than those previously observed and they should make possible a more meaningful comparison between theory and experiment.

Hasegawa, H.: Regarding Dr. Mooser's comment on the line-broadening I would like to point out that we are considering the additional widths associated with the Landau-like levels ($n \geq 1$) in the high magnetic field. Experimentally such a broadening, inherent to the Landau levels as discussed by Prof. Lax in the previous talk, seems to be taking place as shown in Fig. 6 in the preprint of this paper.