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1-5. Band Structure of the Semiconducting Layer Compounds

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Using the tight binding approach, the band structures of GaSe and GaS are derived semiempirically. Their feature is the existence of bands the masses of which are infinitely large along the k_z direction. The valence bands have such a two-dimensional character. The heavy mass at the bottom of the conduction band explains the persistence of *p*-type behavior into the intrinsic range. The conduction band at Γ has the small effective masses. The calculated binding energy of a direct exciton explains experiment well. Most of the observed structures in reflectivity are identified by our band structures.

§ 1. Introduction

A considerable amount of experimental information has recently been accumulated concerning the properties of the three semiconducting layer compounds, GaS, GaSe and GaTe. Particularly, the optical and magneto-optical absorption, reflectivity, galvanomagnetic measurements and photoconductive response have become available for the study of band structures of these compounds. Such theoretical attempts have already been made on the basis of the two-dimensional free electron model[1] and also by the tight binding approach,[2] but these investigations have not clarified the structures of the valence and the conduction bands in detail.

The purpose of the present paper is to derive a reasonably consistent picture of the band structures of these compounds, using the group theoretical analysis and the tight binding approximation. In the following we will first present a summary of the experimental information from which a band picture will be deduced.

(1) The fundamental optical absorption shows that the absorption edges in GaSe and GaTe are direct, whereas that in GaS is indirect.[2,3] There are very strong lines associated with excitons near the edges of GaSe and GaTe. The room temperature reflectivity for GaSe and Gas shows similar structures characterized by three main peaks.[2] The strongest of the three peaks occurs at 4.9 eV in GaSe and 6.1 eV in GaS. Since the direct interband transitions at the critical points in the joint density of states are believed to be responsible for these peaks, the reflectivity data, especially the peaks at 3.63 eV and 4.9 eV in GaSe and at 6.1 eV in GaS, will be used as an aid in establishing the band structures of GaSe and GaS.

(2) Recent measurements on the oscillatory magneto-optical absorption of GaSe have determined an electron-hole reduced mass of $0.14\,m_0$ for the motion parallel to the layer.[4]

(3) The resistivity and Hall measurements on *p*-type GaSe and GaTe crystals with the current parallel to the layer exhibit a high-temperature intrinsic behavior above 600°K.[5,1] The persistence of *p*-type behavior into the intrinsic range indicates that the mobility of holes is larger than that of electrons at high temperatures. In GaSe the activation energy in the intrinsic range is about 1.6 eV, which is smaller than the optically determined energy gap (2.1 eV).

§ 2. The Tight Binding Approach for the π Bands

GaS, GaSe and GaTe crystallize in layers.[6] Each layer is built up of four close-packed sublayers in the sequence of anion-gallium-gallium-anion. Because of the large spacing between two adjacent layers, a two-dimensional band model of a single four-fold layer has been the object of study. The present paper shows, however, that the conduction and higher energy bands are characterized by a three-dimensional band model and that this explains the binding energy of excitons. From the similarity of the crystal structures of the three compounds, we can expect there is no substantial difference in the resultant band structures. Hence we shall confine ourselves to deriving the band structure for one of these and choose hexagonal GaSe, which is most extensively investigated through various kinds of experiments. Then we shall apply the obtained results to the other two compounds, particularly GaS.

Hexagonal GaSe crystal has the space group symmetry D_{3h}^1. The unit cell contains eight

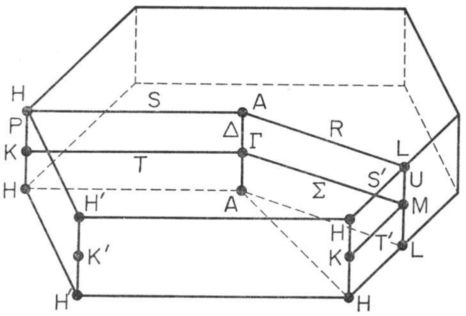

Fig. 1. Brillouin zone for hexagonal GaSe.

atoms, two Ga and two Se from each of the two adjacent four-fold layers. The first Brillouin zone is a thin hexagonal prism as shown in Fig. 1. The Ga and Se atoms possess three and six valence electrons, respectively. These electrons are considered to occupy the $4s$, $4p_x$, $4p_y$ and $4p_z$ orbitals of gallium and selenium. The $4s$, $4p_x$ and $4p_y$ orbitals lie in the layer, while the $4p_z$ orbital is perpendicular to the layer. We call the former σ orbitals and the latter π orbital. It is a useful starting approximation in view of the anisotropic structure of GaSe to classify the energy bands already filled by valence electrons into the σ bands formed by σ orbitals and the π bands formed by π orbitals. In other words, it is assumed that the electrons in the σ bands play a part in forming strong co-planer type of bonds as those in graphite. Thus, all σ bands are fully occupied and expected to lie below the π bands energetically.

On the basis of this approximation it is shown that the highest of the π bands are completely empty and that the bottom of the conduction band and the valence band consist of π bands separately. The nature of the π bands is therefore of interest and in this section we derive the overall structure of the π bands using the tight binding approximation. In doing so, it is assumed that the interactions between four-fold layers are neglected and that within a layer only the resonance integrals between nearest neighbors are important. Then we easily find the energies of the π bands, each of which is characterized by a one-dimensional irreducible representation of the group of $\boldsymbol{k}$. They are

$$\varepsilon_1,\ \varepsilon_3 = 1/2\{\alpha_{\mathrm{Ga}}+\alpha_{\mathrm{Se}}-|\gamma_1| \mp[(\alpha_{\mathrm{Ga}}-\alpha_{\mathrm{Se}}-|\gamma_1|)^2+4|V_{S-G}|^2]^{1/2}\} \quad \text{(1a)}$$

$$\varepsilon_2,\ \varepsilon_4 = 1/2\{\alpha_{\mathrm{Ga}}+\alpha_{\mathrm{Se}}+|\gamma_1| \mp[(\alpha_{\mathrm{Ga}}-\alpha_{\mathrm{Se}}+|\gamma_1|)^2+4|V_{S-G}|^2]^{1/2}\} \quad \text{(1b)}$$

where

$$|V_{S-G}|^2=\gamma_0^2(1+4\cos^2\pi a k_y + 4\cos\sqrt{3}\,\pi a k_x \cos\pi a k_y)\,. \quad (2)$$

The quantities α_{Se} and α_{Ga} are the energies of an electron on the $4p_z$ states in Se and Ga, respectively, and γ_0 and γ_1 are the resonance integrals between the nearest Ga and Se and between the nearest Ga atoms on the adjacent sublayers, respectively.

Each of the four π bands is doubly degenerate. This degeneracy is accidental in the sense that it is caused by the neglect of the interactions between four-fold layers.

§ 3. Semiempirical Band Structures of GaSe and GaS

In the previous section we derived expressions for the energies of the π bands as functions of $\boldsymbol{k}$. The independence of the energies from k_z is due to the omission of the inter-layer interactions. These expressions contain four parameters which are difficult to determine from first principles. Therefore, we will determine them semiempirically as will be shown below. Knowing the values of these parameters, the structure of the π bands is derived as shown in Fig. 2. In this figure the four lowest energy bands correspond to the π bands. In order of increasing energy these are called π_1, π_2, π_3 and π_4, as shown in the figure. Each band at Γ, K and M is labeled by an irreducible representation of the group of $\boldsymbol{k}$. For example, at Γ there are four one-dimensional representations $\Gamma_1{}^{\pm}$, $\Gamma_2{}^{\pm}$ and two two-dimensional ones $\Gamma_3{}^{\pm}$, where the superscripts $\pm$ indicate representations which are symmetric or antisymmetric under reflection with regard to the layer.

The bonding σ bands which are not shown in this figure have been assumed to lie near or below the lowest π band. Thus all the energy bands up to second highest π band, π_3, are completely occupied by the valence electrons and the highest π band, π_4, is empty. Thus, in GaSe the π_3 band corresponds to the valence band the top of which lies at Γ. The fundamental absorption band edge which has been found to be direct must correspond to a transition at Γ. Since the initial state is $\Gamma_2{}^-$, the final state must be $\Gamma_3{}^-$, for the electric field vector of light perpendicular to the c-axis. Therefore, it is concluded that the edge in GaSe corresponds to a transition from the π_3 band to a band other than π_4.

We are now in a position to determine semi-

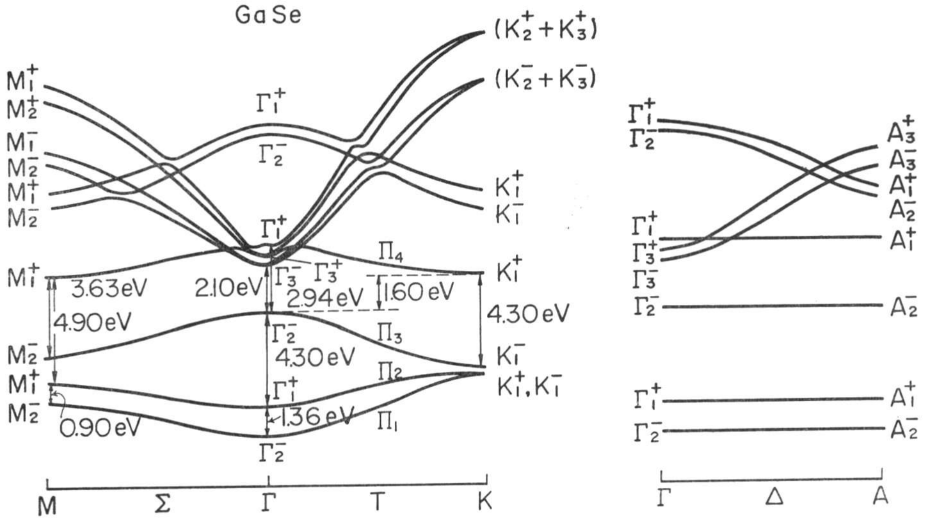

Fig. 2. Band structure of GaSe along $\sum$, T and Δ symmetry directions.

empirically the parameters of the π bands. Since we are concerned only with the relative position of the π bands, the number of parameters to be determined is three, that is, γ_0, γ_1 and $\alpha_{\mathrm{Ga}}-\alpha_{\mathrm{Se}}$. On the other hand, the available experimental data for this purpose are the reflectivity and the thermal energy gap determined from the Hall effect. In connection with direct transitions between unfilled and filled π bands the energies of which are given by $\omega_{4i}(\boldsymbol{k})=\varepsilon_4(\boldsymbol{k})-\varepsilon_i(\boldsymbol{k})(i=1, 2, 3)$, M, L and any point on the symmetry line M–L correspond to saddle points in $\omega_{4i}(\boldsymbol{k})$. Therefore, the joint density of states has logarithmic singularities at these critical points. The direct allowed transitions at these points produce a strong peak in reflectivity. According to group theory a transition between π_2 and π_4 is allowed at any of the above critical points, while those between π_3 and π_4 and between π_1 and π_4 are allowed at a point along the symmetry line M–L except M and L. Therefore, these transitions are responsible for peaks in reflectivity although the intensity of the former is much stronger than that of the latter. Looking at reflectivity data, we assign the strong peak at 4.9 eV to the transition between π_2 and π_4 and the weak peak at 3.63 eV to the transition between π_3 and π_4 at the saddle points. These assignments enable us to determine two parameters and the remaining one is determined from the observed value of thermal energy gap (1.6 eV) in the following way. Since this gap is smaller than that determined optically, we consider that the thermal energy gap corresponds to the energy difference between the top of the valence band and the $K_1{}^+$ state of the π_4 band. Thus the values of parameters $|\gamma_0|$, γ_1 and $\alpha_{\mathrm{Ga}}-\alpha_{\mathrm{Se}}$ are determined to be 0.94, -2.15 and 2.37 eV respectively.

Using these parameters, we can calculate the relative positions of the π bands and their effective masses near symmetry points. Our result shows that $\Gamma_1{}^+$ state of the π_4 band appears about 0.8 eV above the $\Gamma_3{}^-$ state. Therefore, the conduction band has a different character near Γ from that near K. Namely, near Γ it is orbitally doubly degenerate while near the bottom (K) it has the character of the π band.

The surfaces of constant energy for the π bands near Γ and K are circular in the k_x-k_y plane. For the motion in this plane the effective mass of a conduction electron in the $K_1{}^+$ state, $m_{e\perp}(K_1{}^+)$, is 2.64 m_0 and that of a hole in the $\Gamma_2{}^-$ state, $m_{h\perp}(\Gamma_2{}^-)$, is 1.67 m_0. Thus, from the electron-hole reduced mass, we obtain the effective mass of a conduction electron in $\Gamma_3{}^-$ for the motion perpendicular to the c-axis, which is 0.15 m_0. On the other hand, the electron effective mass parallel to the c-axis has not been determined definitely. From a tentative analysis of magneto-optical absorption, however, it is inferred to be 0.36 m_0.

Thus, the overall structure of the conduction and the π bands is derived. This is shown in Fig. 2, where the relative positions of higher energy bands are also shown schematically. On the basis of this energy diagram, we can calculate the peak position corresponding to the transition between π_1 and π_4. The result is given

Table I. Energy of principal reflectivity peaks (in eV).

Transitions	$M_2^-(\pi_1)\rightarrow M_1^+(\pi_4)$	$M_1^+(\pi_2)\rightarrow M_1^+(\pi_4)$	$M_2^-(\pi_3)\rightarrow M_1^+(\pi_4)$
GaSe	5.80 (5.9)	$\underline{4.90}$ (4.9)	$\underline{3.63}$ (3.63)
GaS	6.32 (6.9)	$\underline{6.10}$ (6.1)	4.10 (3.9)

The peaks used for determining the parameters are marked by the underlines.

in the Table I, where the observed values are presented in the parentheses for comparison.

We now turn to a discussion of a band structure of GaS. By a similar argument, the band structure of GaS is also derived semiempirically. Since the parameter γ_1 mainly depends on the orbitals of Ga, we expect it to be nearly the same for GaSe and GaS. The remaining two parameters are determined by assuming that the indirect band edge at 2.6 eV and the reflectivity peak at 6.1 eV correspond to the transition between the Γ_2^- state of the π_3 band and the K_1^+ state of the π_4 band and that between π_2 and π_4 at M, respectively. The obtained values of $|\gamma_0|$ and $\alpha_{\mathrm{Ga}}-\alpha_{\mathrm{S}}$ are 0.63 and 3.72 eV, respectively. Using these values the peak positions in reflectivity are calculated. The results are also given in Table I, together with the observed values. It is concluded from this table that our band structures of GaSe and GaS explain fairly well most of the observed structures of reflectivity in the ranges of 2.0∼6.0 eV and of 3.0∼7.0 eV for GaSe and GaS, respectively.

§ 4. Concluding Remarks

Using the tight binding approach for the π bands, the band structures of GaSe and GaS have been established semiempirically. The outstanding feature of these band structures is the existence of energy bands the masses of which are almost infinitely large along the k_z direction. The valence bands of GaS and GaSe have such a two-dimensional character.

The minima of the conduction bands are also two-dimensional in their character. The heavy electron mass leads us to the conclusion that n-type crystals hardly exist if the donor concentration is not high. The persistence of p-type behavior into the intrinsic range is also explained by the fact that $m_{e\perp}(K_1^+)$ is much larger than $m_{h\perp}(\Gamma_2^-)$.

The conduction band at Γ is doubly degenerate with $m_{e\perp}(\Gamma_3^-)=0.15\,m_0$ and $m_{e//}(\Gamma_3^-)=0.36\,m_0$ though $m_{e//}$ is not definite. Using these values, the binding energy of an exciton is calculated to be 0.027 eV, which is in good agreement with the observed value (0.020 eV), where the static dielectric constants $\epsilon_{//}=7.6$ and $\epsilon_{\perp}=10.2$[7] are used.

The fact that an indirect transition below the direct edge has not been observed in GaSe is due to the following reason: The mixing between the π_4 and higher energy bands in GaSe is less than that in GaS because of the smaller band gap in GaSe. Finally the good agreement with the observed reflectivity strongly supports the assumptions made in deriving our band structures.

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References

1) G. Fischer: Helv. phys. Acta **36** (1963) 317.
2) F. Bassani, D. L. Greenaway and G. Fischer: *Proc. Int. Conf. Semiconductor Physics*, Paris (1964) p. 51.
3) J. L. Brebner and G. Fischer: *Proc. Int. Conf. Semiconductor Physics*, Exeter (1962) p. 760; J. L. Brebner: J. Phys. Chem. Solids **25** (1964) 1427.
4) A. Misu, J. Aoyagi and S. Sugano: private communications.
5) G. Fischer and J. L. Brebner: J. Phys. Chem. Solids **23** (1963) 1363.
6) Z. S. Basinski, D. B. Dove and E. Mooser: Helv. phys. Acta **34** (1961) 373.
7) P. C. Leung, G. Andermann, W. G. Spitzer and C. A. Mead: J. Phys. Chem. Solids **27** (1966) 849.

DISCUSSION

Mooser, E.: We have strong experimental evidence for a direct energy gap in GaSe both from optical absorption and electroluminescence. Within the accuracy of your approximation does your band structure account for such a direct gap? Comment to J. C. Phillips: In view of your statement earlier this afternoon I should like to suggest very strongly, that pseudopotential calculations be carried out on GaSe. The particular features of this layer type structure may well prove to be a good test as to whether the atomic form factors determined from other data can account for the band structures of any kind of crystal structure.

Kamimura, H.: You mentioned that the Hall measurement done by Dr. Fischer was incorrect near the intrinsic range of temperature because of chemical decomposition of GaSe. Thus, in determining the parameters of GaSe, we can no longer use the thermal energy gap, 1.6 eV, which has been determined from his measurement. Therefore, we have only two available data for determining three parameters in the case of GaSe. Fortunately, however, for GaS we have three optical data which are, I believe, more trustable than the transport data. One is the indirect energy gap, 2.6 eV, and another two are reflectivity peaks at 3.9 eV and 6.1 eV. Therefore, we have an alternative procedure to determine three band parameters. Fitting our energy diagram of the π bands to the above mentioned data of GaS, we can determine three parameters of GaS. Their values are: $|\gamma_1|=2.04$, $|\gamma_0|=0.75$, $\alpha_{\mathrm{Ga}}\text{-}\alpha_{\mathrm{S}}=3.87$ in units of eV. Then assuming the same γ_1 for GaSe and GaS, we can determine the remaining two parameters of GaSe from the reflectivity peaks at 3.63 eV and 4.9 eV. The values of three parameters of GaSe thus determined are: $\gamma_1=-2.04$ eV, $|\gamma_0|=0.82$ eV and $\alpha_{\mathrm{Ga}}\text{-}\alpha_{\mathrm{Se}}=2.58$ eV. The resulting band structures of GaSe and GaS do not change significantly from those obtained previously. However, I should like to point out that the K_1^+ state of the π_4 band of GaSe locates 1.9 eV above the top of the valence band instead of the incorrect value of 1.6 eV. Thus I can conclude that the conduction band has nearly the same energy at Γ and K for GaSe. Namely I mean that in GaSe there might not exist the indirect band edge.

Now I am in a position to answer your question. I can say that our band structure of GaSe with new parameters can explain the experimental facts you mentioned within the accuracy of the experimental error.