TWO-DIMENSIONAL INDIRECT EXCITON IN LAYER-TYPE SEMICONDUCTOR GaSe

H. Kamimura and K. Nakao
Department of Physics, University of Tokyo, Tokyo, Japan

and

Y. Nishina
The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan
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Evidence for the presence of two-dimensional indirect excitons is presented in terms of the absorption spectra in GaSe. The phonon and exciton parameters at the K point are determined.

Measurements of the absorption spectrum of β-GaSe below the direct edge have revealed a set of structures in the energy range from 1.70 to 2.0 eV. A remarkable feature of these structures is the presence of a plateau over the energy range of 0.12 eV. It is shown in this paper that this plateau may be interpreted only in terms of a two-dimensional indirect exciton. To our knowledge this is the first report on the observation of a two-dimensional exciton.

β-GaSe is a layer-type semiconductor with a hexagonal crystal structure. The band structure has been calculated by Kamimura and Nakao,[1] and also by Bassani and Pastori Parravicini,[2] with the tight-binding approximation. Particularly the band model proposed by the former group indicates the possible existence of an indirect edge. This theoretical prediction has been verified experimentally by Brebner, Mooser, and Aulich,[3] and by Nishina, Kuroda, and Fukuroi.[4] Figure 1 shows the details of the band structure assigned by Kamimura and Nakao.[1] The valence and conduction bands, denoted by π_3 and π_4, respectively, may be regarded as two-dimensional in their character in the sense that their masses along the direction perpendicular to the layer (c axis) are very large. An indirect transition is allowed between the top of π_3 and the bottom of π_4 ($\Gamma_2^- \rightarrow K_3^+$) for the electric field vector of light parallel to the c axis ($\vec{E} \parallel c$). For light incident normal to the layer ($\vec{E} \perp c$), however, such transitions are forbidden. This selection rule comes from symmetry of the conduction and valence bands at Γ and K points. On the basis of these assignments on the band edges, only the K_3^+ mode of phonon contributes to the indirect transition. Group-theoretical consideration of the crystal structure of β-GaSe shows that there exist four of the K_3^+ modes in β-GaSe.

According to Elliott,[5] the transition probability for the indirect transition to an excitonic state $(\vec{K}, n)$ is proportional to

$$(n_{\vec{K}} + \tfrac{1}{2} \mp \tfrac{1}{2}) |\varphi_n(0)|^2 \delta(h\nu - E_g + E_{\vec{K},n} \pm \hbar\omega_{\vec{K}}) \quad (1)$$

for the absorption (upper sign) and emission (lower sign) of a phonon. Here $h\nu$ is the photon energy, $\hbar\omega_{\vec{K}}$ the phonon energy, $n_{\vec{K}}$ the phonon population number, E_g the indirect band gap, $E_{\vec{K},n}$ the energy of the excitonic state $(\vec{K},n)$, and $\varphi_n(\vec{r})$ the so-called envelope function of the Wannier indirect exciton.

For a two-dimensional bound exciton which has

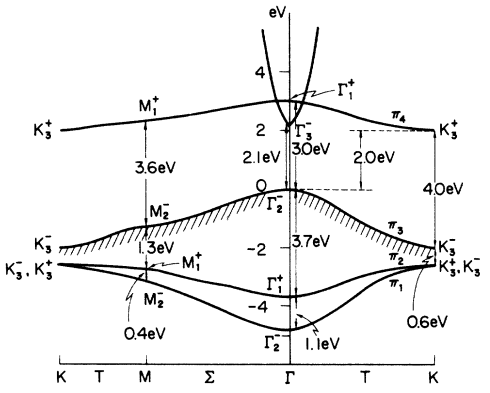

FIG. 1. The band structure of β-GaSe (after Ref. 1). The indirect transition occurs between the top of valence band π_3 at Γ and the bottom of conduction band π_4 at K. [Our assignments of the π bands at the K point in Ref. 1 are incorrect. The correct assignments should be as follows: K_2^- for π_1, K_2^+ for π_2, K_3^- for π_3, and K_3^+ for π_4 bands, respectively. Consequently K_1^+ and K_1^- in the text of Ref. 1 should be read as K_3^+ and K_3^-, respectively.] According to this assignment of the band edges, the following two processes contribute to the indirect transition: In one process the electron-hole pair is created at the Γ point followed by the scattering of the electron to K by phonons of the K_3^+ mode. In another process the pair is created at K followed by the scattering of the hole to Γ by the K_3^+ phonons.

the wave vector $\vec{K}(K_x,K_y)$, one obtains[6]

$$E_{\vec{K},n}=\frac{\hbar^2(\vec{K}-\vec{K}_0)^2}{2M}-\frac{R}{(n+\frac{1}{2})^2}, \quad (2)$$

and

$$|\varphi_n(0)|^2=1/\pi a^2(n+\tfrac{1}{2})^3, \quad (3)$$

where $n=0,1,2,\cdots$; R is the effective Rydberg constant; a the effective Bohr radius; and $\vec{K}_0$ the wave vector corresponding to the K point in the Brillouin zone.

Using the fact that the density of states in a single two-dimensional excitonic band is independent of energy,[7] one obtains the absorption coefficient as

$$\alpha_n(h\nu)\propto(n_{\vec{K}_0}+\tfrac{1}{2}\mp\tfrac{1}{2})\frac{1}{\pi a^2(n+\frac{1}{2})^3}\times S\left(h\nu-E_g+\frac{R}{(n+\frac{1}{2})^2}\pm\hbar\Omega_i\right), \quad (4)$$

where $S(x)$ is the step function such that $S(x)=1$ for $x>0$ and $S(x)=0$ for $x<0$, and Ω_i is the phonon frequency of the ith K_3^+ mode at K point. Thus the contribution to the absorption from each excitonic band has relative magnitude given by $|\varphi_n(0)|^2\propto(n+\frac{1}{2})^{-3}$ $(n=0,1,2,\cdots)$, and begins at energies $E_g-R(n+\frac{1}{2})^{-2}\mp\hbar\Omega_i$. It should be emphasized that the dependence of α_n on n and its independence of $h\nu$ in Eq. (4) is in remarkable contrast with the corresponding expression for the three-dimensional indirect exciton which is proportional to[5] $n^{-3}(h\nu-E_g+Rn^{-2}\pm\hbar\Omega_i)^{1/2}$ with $n=1, 2,\cdots$.

The samples used in this investigation were grown by the Bridgman method. Their typical dimensions were 5.9×9.9 mm in the c plane and 2.1 mm along the c axis. The monochromatic radiation was sent along the c plane. The plane of incidence was optically finished with SeO_3 powder and silk cloth. The surface irregularity was examined under a microscope. The resolution of the Perkin-Elmer spectrometer system was about 3 meV in the present wavelength range. With correction for the surface reflection and scattering, the observed absorption coefficient is shown in Fig. 2(a) for the different polarizations. The sharp rise of the curve beyond 2 eV is the tail of the direct excitonic absorption at the the Γ point.

The step function in Eq. (4) corresponds to the plateau between 1.88 and 2.0 eV in the curve of Fig. 2(a). Such a characteristic singularity in the absorption spectra has not been observed in the indirect absorption edge of ordinary semiconductors.[8] In other words, the absorption coefficient for ordinary three-dimensional indirect excitons has the square root dependence on photon energy and such an expression cannot explain the plateau, as shown in Fig. 2(b). These facts lead to the conclusion that the observed plateau represents the characteristics of a two-dimensional indirect exciton.

Besides the plateau there exist four distinct absorption steps below 1.88 eV. The observation of these four steps is consistent with the group-theoretical prediction on the number of phonon modes participating in this indirect transition. These steps represent only the emission of four phonons because the phonon absorption process is negligible at 4.2°K. The frequencies of the four K_3^+ phonons are determined by the well-established procedure.[9] Namely, their differences are determined as

$$\hbar\Omega_2-\hbar\Omega_1=0.04\pm0.01 \text{ eV},$$

$$\hbar\Omega_3-\hbar\Omega_1=0.08\pm0.01 \text{ eV},$$

$$\hbar\Omega_4-\hbar\Omega_1=0.14\pm0.01 \text{ eV}.$$

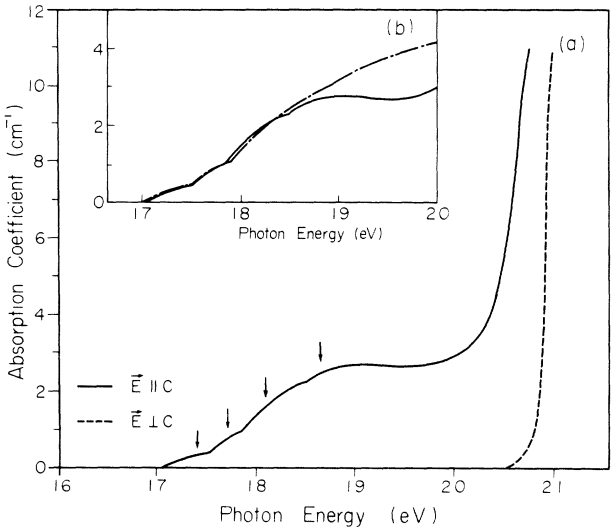

FIG. 2. (a) The absorption coefficient of β-GaSe at 4.2°K for two polarizations of the electric field of the incident radiation. The observed curve for $\vec{E}\parallel c$ (solid line) is in complete agreement with Eq. (5), corresponding to the two-dimensional indirect exciton. From this analysis the energies of $E_g-4R+\hbar\Omega_i$ with $i=1, 2, 3, 4$ have been determined, which are indicated by the four arrows. The absence of the indirect absorption spectra for $\vec{E}\perp c$ verifies our theoretical prediction on the selection rule described in the text. (b) The absorption coefficient for the three-dimensional indirect exciton is shown by the dash-dotted line and compared with the observed one shown by the solid line.

Then the effective Rydberg constant R is determined to be 50 meV from the difference between the energy for the step-wise singularity and the threshold energy for the transition to the continuum of the unbound two-dimensional indirect exciton, where the absorption coefficient for the continuum is proportional to $(h\nu - E_g - \hbar\Omega_i)$.

Now we can calculate the total absorption coefficient for the indirect transitions due to the four K_3^+ phonons and compare it with the observed one. Here one may neglect the contributions from the $n=1$ and higher-n excitonic states, because the magnitude of α_n for $n \geq 1$ is less than 1/27 of that for $n=0$ as shown in Eq. (4). Also the effects of the lifetime broadening of the excitonic states are taken into account. This broadening is estimated in a phenomenological way by replacing the $\delta(x)$ function in Eq. (1) by a function of Lorentzian form, $f(x) = \gamma/\pi(x^2+\gamma^2)$, with a damping constant γ. Thus the total absorption coefficient for the indirect transitions in β-GaSe is expressed by the following form:

$$\alpha_T(h) = \sum_{i=1}^{4} A_i \left\{ \frac{1}{\pi} \tan^{-1}\left[\frac{h\nu - E_g + 4R - \hbar\Omega_i}{\gamma} \right] + \frac{1}{2} \right\}. \tag{5}$$

The height of the absorption steps in Fig. 2(a) determines the magnitudes of the A_i in Eq. (5), namely,

$$A_1 = 0.3 \text{ cm}^{-1}, \quad A_2 = 0.6 \text{ cm}^{-1},$$

$$A_3 = 1.2 \text{ cm}^{-1}, \quad A_4 = 0.6 \text{ cm}^{-1}.$$

With the choice of $\gamma = 13$ meV and $E_g + \hbar\Omega_1 = 1.93 \pm 0.01$ eV, one may obtain complete agreement between the calculated and observed line shapes below 2.0 eV. It should be noted that the existence of the plateau does not depend on the various parameters in Eq. (5) except that the length of the plateau is determined by R which is much greater than γ.

Finally, we must compare this result with that obtained for the three-dimensional indirect exciton. As we have already stated, the absorption coefficient for the three-dimensional indirect exciton associated with each phonon emission or absorption process has a square-root dependence on photon energy and thus such a model cannot explain the observed plateau. This is clearly seen in Fig. 2(b) in which the absorption coefficient for the three-dimensional indirect exciton is shown by the dash-dotted line. The parameters $\hbar\Omega_i$, A_i, R, and γ for the three-dimensional model have been chosen so as to reproduce the observed four steps as closely as possible.

Thus, it is concluded from Figs. 2(a) and 2(b) that the observed plateau for $1.88 \text{ eV} < h\nu < 2.0$ eV is characterized only by the two-dimensional indirect exciton, and not by any choice of the parameters of the three-dimensional one.

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