PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN **49** (1980) SUPPL. A p. 371–374

EXCITONIC EFFECTS ON OPTICAL TRANSITIONS TO A D$^-$ BAND IN DOPED SEMICONDUCTORS

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Theory of optical spectra of donors in semiconductors in low and intermediate concentrations is developed by taking account of the excitonic interaction and disorder. It is shown that inhomogeneous broadening due to a localized exciton in a random system contributes to the formation of wide spectral tail in low energy region, while homogeneous broadening due to transfer of a delocalized exciton which is mixed into excited states of a donor contributes to a broad structure in high energy region.

1. Introduction

As the donor concentration in semiconductors increases towards the metal-insulator transition, optical spectra of donors change their features from sharp lines to smooth ones via broadened structures of the line spectra and the absorption edges shift to lower energy with increasing concentration [1,2,3]. In the present paper we calculate the overall lineshape of absorption spectra of donors in the low and intermediate concentration ranges by taking into account the excitonic interaction between a D$^-$ ion and a hole left at an excited donor, compare them with experiments for Ge:As and clarify the origin of overall optical structures. In §2 the outline of the present theoretical treatment is described. The final state of transitions is expressed by the mixed state of an excited atom and the D$^-$ band[4]. The electron-hole interaction is introduced in the form that the energy of D$^-$ levels is lowered by its interaction energy with a hole. Further the effect of disorder due to random distribution of donor atoms are treated by Matsubara-Toyozawa approximation [5]. In this view our meanfield treatment is complimentary to the cluster method recently developed by Bhatt and Rice [6]. In order to investigate the interplay between the spatial variation of an exciton energy and the migration of an exciton, the local density of states is calculated in §3. In §4 it is shown that the low energy tail region of spectra is due to the inhomogeneous broadening caused by the variation of a localized exciton energy. In higher energy region, the broadened excitations of a donor are superposed on the spectra to a D$^-$ band homogeneously broadened due to the delocalization effect of an exciton among D$^-$ ions. Finally the calculated line shape for Ge:As is compared with experimental results.

2. Formulation

We consider a N donor system with N electrons. In the effective mass approximation, the Hamiltonian for this system is given by

$$H=\sum_i\left(\frac{\mathbf{p}_i^{\,2}}{2m}-\sum_j\frac{e^2}{\kappa|\mathbf{r}_i-\mathbf{R}_j|}\right)+\sum_{i<j}\frac{e^2}{\kappa|\mathbf{r}_i-\mathbf{r}_j|}\quad, \tag{1}$$

where κ represents the static dielectric constant and $\mathbf{R}_j$ the position **of j-th impurity site. For simplicity, we have taken the effective mass approximation with an isotropic mass. In the low and intermediate concentration regions, the tight binding picture is well applied.** As for the ground state of this system, which we denote by Ψ_g, we simply assume that all the electrons occupy the 1s state in each donor atom. By absorbing photon with energy below the donor ionization energy, one electron is excited to a donor excited state in the same impurity, or to a D^- state in other impurities by the overlap effects. Thus the final state corresponds to the mixed state of two kinds of electron configurations [4]. The one type is the state where an excited electron occupies an excited state within the same donor which is denoted as 0-th site hereafter. The other type is the state where an electron at 0-th site is charge-transferred to a neutral donor site leaving a hole at 0-th site and makes a D^- ion state at the transferred site. In the former case the N-electron configuration can be written by the Slater determinant constructed from the donor wave function of the excited state α at 0-th site and the ground state 1s wave functions in other (N-1) donor atoms. We denote this state by $\Psi_\alpha(0)$. In the latter case, the N-electron state is given by the anti-symmetrized form of the wave function constructed from the two electron wave function of a D^- ion, for example, at n-th site and the 1s wave functions in other (N-2) impurity sites. This state is denoted by $\Psi_{D^-}(n)$. Now we denote the matrix elements of the Hamiltonian (1) with regard to the states, $\Psi_\alpha(0)$ and $\Psi_{D^-}(n)$ in the following way.

$$\begin{aligned}&\langle\Psi_\alpha(0)|H|\Psi_\alpha(0)\rangle=\varepsilon_\alpha-\varepsilon_{1s}+E_g,\quad \langle\Psi_{D^-}(n)|H|\Psi_\alpha(0)\rangle=V_{no}(\alpha),\\ &\langle\Psi_{D^-}(n)|H|\Psi_{D^-}(n)\rangle=\varepsilon_n-\varepsilon_{1s}+E_g,\quad \langle\Psi_{D^-}(n)|H|\Psi_{D^-}(m)\rangle=V_{nm}(D^-),\end{aligned} \tag{2}$$

where $E_g=\langle\Psi_g|H|\Psi_g\rangle$ is the ground state energy, taken to be zero hereafter and we have neglected all the transfer integrals involving the 1s states. ε_α is the energy of an excited state α, $V_{nm}(D^-)$ and $V_{on}(\alpha)$ represent transfer integrals and ε_n is given by

$$\varepsilon_n=\varepsilon_{D^-}-\frac{e^2}{\kappa R_n}\quad, \tag{3}$$

where $(\varepsilon_{D^-}+\varepsilon_{1s})$ is the energy of an isolated D^- ion, R_n is the distance between n-th site and a hole at 0-th site and the second term is due to the attractive interaction between a hole and a D^- ion. Throughout the paper, we call this D^- ion-hole pair an exciton.

The absorption coefficient $\alpha(E)$ for photon energy E is calculated from the following formula

$$\alpha(E)=N\frac{4\pi e^2}{n\hbar c}E\cdot\mathrm{Im}\langle\Psi_g|M\frac{1}{E-i\eta-H}M^\dagger|\Psi_g\rangle\ , \tag{4}$$

where n is the refractive index and M is an operator for the optical transition. The matrix elements of M between Ψ_g and the final state are expressed by two quantities,

$$\langle\Psi_\alpha(0)|M^\dagger|\Psi_g\rangle=M_\alpha,\qquad \langle\Psi_{D^-}(n)|M^\dagger|\Psi_g\rangle=M_n. \tag{5}$$

In the calculation of $\alpha(E)$, we use the Matsubara-Toyozawa approximation [5] for treating random variables $V_{on}(\alpha)$ and $V_{nm}(D^-)$. The

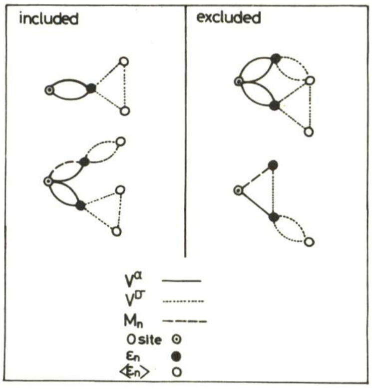

Fig.1 Typical diagrams included and excluded in the calculation of $\alpha(E)$: Site energy used in the calculation is also shown

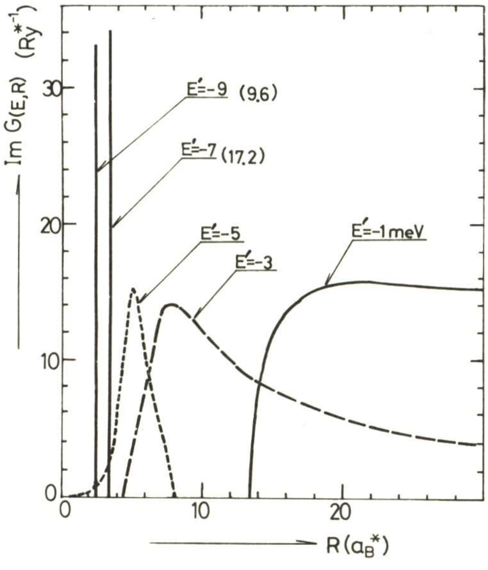

Fig.2 Local density of states of a D^- band for the concentration $p=0.5$ ($N=4\times10^{16}cm^{-3}$), where p is defined as $p=64\pi Na_B^{*3}$: The number in parenthesis shows the intensity of δ-function

diagrams which are included and excluded are shown schematically in Fig.(1). Further we take only diagonal part of the Green function $G_{nn}(E,R)$, which is defined by

$$G_{nn}(E,R)=<\Psi_{D^-}(n)|\frac{1}{E-i\eta-H_{D^-}}|\Psi_{D^-}(n)>, \quad (6)$$

where H_{D^-} corresponds to Hamiltonian for a D^- band spanned by a set of $\Psi_{D^-}(n)$, whose matrix elements are represented by the second line of eq.(2). As regards ε_n appeared in $G_{nn}(E,R)$, we use eq.(3) only for n-th site, and for other sites m, we use the appropriate value of ε_m averaged over sites around n-th site. Further as for the functional forms of M_n, $V_{0n}(\alpha)$ and $V_{nm}(D^-)$, we calculate these with use of hydrogen-like wave functions for donor excited states and Chandrasekhar type wave function for a D^- ion [7,8].

3. Local Density of States

In this section we investigate the interplay between the effects of transfer and excitonic interaction in optical transitions to the D^- band. For this purpose we calculate the local density of states for a D^- band in the presence of a hole at 0-th site, which is defined by Im $G_{nn}(E,R)$. Here Im $G_{nn}(E,R)$ is related to the density of states $D(E)$ of a D^- band by $D(E) = \int \mathrm{Im}\, G_{nn}(E,R)dR/\pi$. Numerical results for certain values of energy E are shown in Fig.(2) as a function of the distance R from a hole at 0-th site. For a very low energy, for example $E' = -9$meV in Fig.(2)(E' is related to the photon energy E by $E = E' - \varepsilon_{1s}$), an exciton is localized in the region around R_0, where R_0 is determined by the relation of $E = \varepsilon_{D^-} - e^2/\kappa R_0$. This is because the energy difference due to the excitonic interaction between two different sites is larger than the transfer integral $V_{nm}(D^-)$. On the other hand in the higher energy region of E, the range of R becomes extended as seen in Fig.(2) and an exciton in which a hole is kept fixed at 0-th site is delocalized among D^- ions.

Thus the transfer effect is superior to the variation of site energy ε_n due to the excitonic effect in this region.

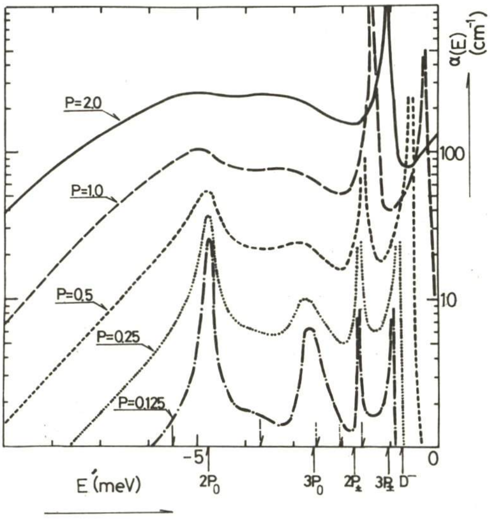

Fig.3 Calculated optical absorption spectra for Ge:As. The lower edge of a D⁻ band without exciton effect and excitation energies of an isolated donor are shown by arrows

4. Numerical Results and Discussion

In Fig.(3), we present calculated optical absorption spectra for Ge:As for various concentrations p (where p is defined as $p = 64\pi N a_B^{*3}$). As p increases, the low energy tail grows and the peaks corresponding to transitions to $2p_0$ and $3p_0$ states show broadening and small shift to lower energy side. The broadening and shift of peaks are due to interaction with a D^- band via $V_{0n}(\alpha)$, while the appearence of low energy tail due to excitonic effects. Recently, detailed experimental observation [3] has been made for Ge:As for $p \simeq 0.5$, and it has been found that the energy dependence of $\alpha(E)$ in tail region is approximately expressed as $\exp(E/A)$, where A is $0.091Ry^*$, just like the Urbach tail. In our calculation, $\alpha(E)$ in tail region also shows the exponential dependence on E as shown in Fig.(3), where theoretical value of A is $0.116Ry^*$ for $p = 0.5$. Thus the present theory explains the observed tail spectra satisfactorily. As for the high energy region around $2p_0$ and $3p_0$ transitions, the calculated result also shows a fairly good agreement with experimental result [1], while in higher energy region around $2p_\pm$ and $3p_\pm$ transitions, our tight binding approximation cannot describe the system appropriately.

Acknowledgments

The authors wish to thank Professors S. Narita, Y. Nishida and Dr. M. Kobayashi for valuable discussions, especially for showing them experimental data prior to publications.

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