increases on cooling. This behavior is the case for most semiconductors.

IV. SUMMARY AND CONCLUSIONS

The electrical properties of several polycrystalline samples of β-Ag_2Se with identical x-ray diffraction patterns have been studied as a function of temperature. The results suggest the existence of two phases with energy gaps at 0°K of 0.07 eV and 0.18 eV, respectively. The latter value agrees with the figure reported by Baer *et al.*[7] for the β_2 phase. The threshold of optical absorption due to direct band-to-band transitions was 0.13 eV at 5°K. The probable existence of a Burstein shift of the absorption edge suggests that these optical data correlate best with the value of $E_0=0.07$ eV. The optical-absorption data also indicate that the energy increases on cooling.

It appears that further study of the energy gap of β-Ag_2Se is warranted. It would be of primary importance to make measurements of the temperature variation of the electrical properties on well-defined single-crystal samples if they can be prepared. Such studies would certainly be of great assistance in defining the semiconductor properties of β-Ag_2Se in general, and in providing further information on the β_2 phase in particular.

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Exciton-Donor Complexes in Semiconductors*

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The binding energy of an exciton bound to a neutral donor is estimated using the quantum-mechanical variational principle. We obtain the dissociation energy of an exciton-donor complex as a function of the ratio of the effective mass of the electron to that of the hole. The theoretical analysis is carried out within the framework of the effective-mass approximation, assuming a simple model of a semiconductor with parabolic energy bands.

I. INTRODUCTION

A CONSIDERABLE amount of optical data in semiconductors can be interpreted as resulting from the existence of excitons bound to impurity centers in semiconductors. Haynes[1] studied the photoluminescence of Si of known donor and acceptor concentrations and interpreted the observed spectral lines as resulting from complexes involving an exciton associated with a neutral donor or with a neutral acceptor. From his results one finds that the dissociation energy of the exciton–neutral-donor complex is nearly 0.13 times the ionization energy of the donor. This ratio is independent of the chemical nature of the impurity atoms (Sb,P,As,Bi). Several authors[2–6] also observed similar spectra in the photoluminescence of defect-exciton complexes in II–VI compounds, namely ZnS, CdS, ZnSe, and CdTe. They find the ratio of the dissociation energy[7] of the complex to the ionization energy of the donors to be about 0.20. No detailed theoretical calculations of the binding energy of the ground states of such complexes have yet been reported. The object of the present work is to attempt an investigation of this subject. We have assumed that the effective-mass approximation is valid and that the constant energy surfaces are spherical. Making use of a method due to James and Coolidge[8] for the calculation of energy matrix elements, we have obtained the ratio of the dissociation energy of the exciton–neutral-donor complex to the ionization energy of the neutral donor as a function of σ, the ratio of effective mass m_e of the electron to the effective mass m_h of the hole. Our calculations of these energy ratios for the cases of Si and CdS yield the values 0.13 and 0.125, respectively, which compare not too unfavorably with the corresponding experimental results, namely 0.13 and 0.20. The next section is

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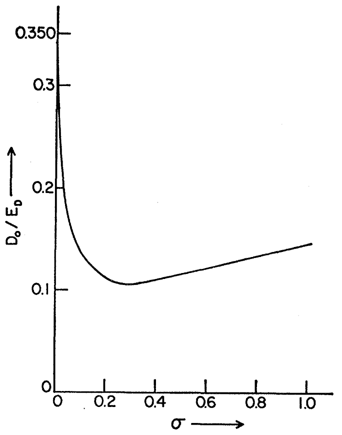

FIG. 1. Dissociation energy of a donor-exciton complex as a function of $\sigma = m_e/m_h$.

devoted to the calculation of the dissociation energy of the system we consider. The results are summarized by the graph in Fig. 1.

II. CALCULATIONS

The exciton–neutral-donor complex is regarded as consisting of a singly charged donor, two electrons and a hole, all interacting with one another through Coulomb forces. The singly charged donor is taken to be fixed at the position a and the coordinates of the hole and of the electrons are designated by b, 1, 2, respectively. The model Hamiltonian of the system is written in the form

$$\mathcal{H} = -\frac{h^2}{2m_h}\nabla_h^2 - \frac{h^2}{2m_e}\nabla_1^2 - \frac{h^2}{2m_e}\nabla_2^2 + \frac{e^2}{KR} - \frac{e^2}{Kr_{a1}} - \frac{e^2}{Kr_{a2}} - \frac{e^2}{Kr_{b1}} - \frac{e^2}{Kr_{b2}} + \frac{e^2}{Kr_{12}}. \quad (1)$$

In the above equation the first, second, and third terms are the kinetic energies of the hole, of electron 1, and of electron 2; R is the distance between a and b, the positions of the donor and of the hole; K is the static dielectric constant of the host crystal. The distance between the position a and electron 1 is denoted by r_{a1}. Other distances are defined in a similar fashion.

We take the unit of length to be $a_0^* = K\hbar^2/m_e e^2$ and the unit of energy as e^2/Ka_0^* so that, in these units,

$$\mathcal{H} = -\tfrac{1}{2}\sigma\nabla_h^2 - \tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 + \left[\frac{1}{R} - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}}\right]. \quad (2)$$

We now transform the Hamiltonian using parabolic coordinates defined by

$$\lambda_1 = \frac{r_{a1}+r_{b1}}{R}, \quad \mu_1 = \frac{r_{a1}-r_{b1}}{R},$$
$$\lambda_2 = \frac{r_{a2}+r_{b2}}{R}, \quad \mu_2 = \frac{r_{a2}-r_{b2}}{R}, \quad (3)$$
$$\rho = 2r_{12}/R.$$

The transformed Hamiltonian can be put into the form

$$\mathcal{H} = -\tfrac{1}{2}\sigma\nabla_h^2 + H, \quad (4)$$

where

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 + \frac{1}{R}\left\{1 + \frac{2}{\rho} - \frac{4\lambda_1}{\lambda_1^2-\mu_1^2} - \frac{4\lambda_2}{\lambda_2^2-\mu_2^2}\right\}. \quad (5)$$

We are interested in the lowest eigenvalue W of the Hamiltonian $\mathcal{H}$ which we estimate by applying the variational principle. If the total wave function of the system is ψ, we have

$$W = \langle\psi|\mathcal{H}|\psi\rangle, \quad (6)$$

where ψ is assumed to be normalized. The simplest form of the wave function ψ is a product of two wave functions, one of which depends on the coordinates **R** and the other on the coordinates λ_1, μ_1, λ_2, μ_2, and ρ such as

$$\psi = f(\mathbf{R})g(\lambda_1,\mu_1,\lambda_2,\mu_2,\rho). \quad (7)$$

We can immediately write

$$W = -\tfrac{1}{2}\sigma\langle fg|\nabla_h^2|fg\rangle + \langle f|V(R)|f\rangle, \quad (8)$$

where

$$V(R) = \langle g|H|g\rangle. \quad (9)$$

Following James and Coolidge[8] we choose for g a five-parameter wave function of the form

$$g = N^{-1/2}\sum_{mnjkp} C_{mnjkp}\psi_{mnjkp}, \quad (10)$$

where

$$\psi_{mnjkp} = (2\pi)^{-1}\exp[-\delta(\lambda_1+\lambda_2)] \times(\lambda_1^m\lambda_2^n\mu_1^j\mu_2^k\rho^p + \lambda_1^n\lambda_2^m\mu_1^k\mu_2^j\rho^p). \quad (11)$$

The factor N is determined by the normalization condition

$$\langle g|g\rangle = 1, \quad (12)$$

and δ and C_{mnjkp} are variational parameters.

It can be easily shown that

$$V(R) = A/R^2 - B/R, \quad (13)$$

where

$$A = \frac{1}{N_0}\sum_{\substack{m_a,n_a,j_a,k_a,p_a\\ m_b,n_b,j_b,k_b,p_b}} C_{m_a n_a j_a k_a p_a}C_{m_b n_b j_b k_b p_b} \times\{u_{ab}^{(1)} + u_{ab}^{(2)} + u_{ab}^{(3)} + u_{ab}^{(4)}\}, \quad (14)$$

with

$$u_{ab}{}^{(1)}=-(1/64)\{[(n_a-n_b)^2-(k_a-k_b)^2+(n_a+n_b)$$
$$-(k_a+k_b)+(p_a-p_b)(n_a-n_b-k_a+k_b)]X(00000)$$
$$-4\delta X(01000)-[(n_a-n_b)^2-(n_a+n_b)]X(0-2000)$$
$$+[(k_a-k_b)^2-(k_a+k_b)]X(000-20)+[(p_a-p_b)^2$$
$$+(p_a+p_b)+(p_a-p_b)(n_a-n_b+k_a-k_b)][X(0200-2)$$
$$-X(0002-2)]-(p_a-p_b)(n_a-n_b-(k_a-k_b))$$
$$\times[X(2000-2)+X(0020-2)]+2(p_a-p_b)(n_a-n_b)$$
$$\times X(1-111-2)-2(p_a-p_b)$$
$$\times(k_a-k_b)X(111-1-2)\}. \quad (15)$$

Here, $X(01000)$ stands for $X(m_a+m_b,\, n_a+n_b+1,\, j_a+j_b,\, k_a+k_b,\, p_a+p_b)$, where

$$X(m,n,j,k,p)=\frac{1}{4\pi^2}\int(\lambda_1{}^2-\mu_1{}^2)\exp[-2\delta(\lambda_1+\lambda_2)]$$
$$\times\lambda_1{}^m\lambda_2{}^n\mu_1{}^j\mu_2{}^k\rho^p d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2.$$

The other quantities have similar meanings. $u_{ab}{}^{(2)}$ is obtained from $u_{ab}{}^{(1)}$ by making the substitution $[m_a\rightleftarrows n_a,\, j_a\rightleftarrows k_a]$. Similarly $u_{ab}{}^{(3)}$ is obtained from $u_{ab}{}^{(1)}$ by $[m_b\rightleftarrows n_b,\, j_b\rightleftarrows k_b]$ and $u_{ab}{}^{(4)}$ is obtained from $u_{ab}{}^{(1)}$ using the transformations $[m_a\rightleftarrows n_a,\, j_a\rightleftarrows k_a,\, m_b\rightleftarrows n_b,\, j_b\rightleftarrows k_b]$. The quantity N_0 in Eq. (14) designates the sum

$$N_0=\sum_{\substack{m_a,n_a,j_a,k_a,p_a,\\ m_b,n_b,,j_bk_b,p_b}} C_{m_an_aj_ak_ap_a}C_{m_bn_bj_bk_bp_b}$$
$$\times\{S_{ab}{}^{(1)}+S_{ab}{}^{(2)}+S_{ab}{}^{(3)}+S_{ab}{}^{(4)}\}, \quad (16)$$

where

$$S_{ab}{}^{(1)}=(1/64)[X(02000)-X(00020)]. \quad (17)$$

To obtain $S_{ab}{}^{(2)}$, $S_{ab}{}^{(3)}$, $S_{ab}{}^{(4)}$, we make changes in $S_{ab}{}^{(1)}$ similar to those used above for obtaining $u_{ab}{}^{(2)}$, $u_{ab}{}^{(3)}$, and $u_{ab}{}^{(4)}$.

The parameter B is defined by

$$B=\frac{1}{N_0}\sum_{\substack{m_a,n_a,j_a,k_a,p_a\\ m_b,n_b,j_b,k_b,p_b}} C_{m_an_aj_ak_ap_a}C_{m_bn_bj_bk_bp_b}$$
$$\times\{v_{ab}{}^{(1)}+v_{ab}{}^{(2)}+v_{ab}{}^{(3)}+v_{ab}{}^{(4)}\}, \quad (18)$$

where

$$v_{ab}{}^{(1)}=-(1/64)\{X(02000)-X(00020)+$$
$$+2X(0200,-1)-2X(0002,-1)-8X(01000)\}. \quad (19)$$

The quantities $v_{ab}{}^{(2)}$, $v_{ab}{}^{(3)}$, and $v_{ab}{}^{(4)}$ are obtained in the same manner as $u_{ab}{}^{(2)}$, $u_{ab}{}^{(3)}$, and $u_{ab}{}^{(4)}$ from $u_{ab}{}^{(1)}$. The normalization constant occurring in Eq. (10) and defined by Eq. (12) is connected to N_0 by

$$N=N_0R^6. \quad (20)$$

The function g given in Eq. (10) is a function of R through the normalization constant N and therefore is proportional to the inverse third power of R. We take $f(R)=R^{-2}F(R)$ where $F(R)$ is the eigenfunction of the operator

$$-\tfrac{1}{2}\sigma\frac{d^2}{dR^2}+\frac{A}{R^2}-\frac{B}{R}$$

belonging to its lowest eigenvalue. This completes the choice of the form of the variational wave function. The expectation value W of $\mathcal{H}$ is given by the expression

$$W=-(4B^2E_D/\sigma)[1+\{1+(8A/\sigma)\}^{1/2}]^{-2}, \quad (21)$$

where we have restored the original cgs units. The symbol

$$E_D=(m_ee^4/2K^2\hbar^2) \quad (22)$$

stands for the ionization energy of the donor. The dissociation energy D_0 of the complex is

$$D_0=-W-E_D-E_{\text{ex}}, \quad (23)$$

where E_{ex} is the binding energy of the exciton, which in our model is simply

$$E_{\text{ex}}=(1+\sigma)^{-1}E_D. \quad (24)$$

Making use of Eqs. (21), (22), and (24), Eq. (23) simplifies to

$$(D_0/E_D)=(4B^2/\sigma)[1+\{1+(8A/\sigma)\}^{1/2}]^{-2}$$
$$-1-(1+\sigma)^{-1}. \quad (25)$$

Here A and B depend on the variational parameters δ and C_{mnjkp}. The five sets of values of $mnjkp$ which we have chosen for our computation are (00000), (00020), (00110), (10000), (00001). In actual calculation we have kept the first coefficient C_{00000} equal to unity and varied the parameters δ and the other coefficients, namely C_{00020}, C_{00110}, C_{10000}, and C_{00001} in order to obtain the minimum value of W or maximum value of D_0. The calculation was performed for various values of the mass ratio σ. The maximized value of D_0/E_D was then plotted as a function of σ and displayed in Fig. 1.

Finally we make the following remarks. From Feynman's theorem one can easily demonstrate that (W/E_D) is a monotonically increasing[9] function of σ where W is the *exact* ground-state energy of the complex. Our variational calculations give a result which agrees with this condition. Now (D_0/E_D) is the difference of the two monotonically decreasing functions $(-W/E_D)-1$ and $(1+\sigma)^{-1}$. Thus the graph of (D_0/E_D) in Fig. 1 is not a monotomic function of σ. Our calculations have not been extended beyond $\sigma=1.0$ because the trial wave function is not appropriate for large values of σ.

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[9] See Ref. 1, footnote 7.