Binding energies of simple isoelectronic impurities in II-VI semiconductors

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(Received 19 March 1992; revised manuscript received 26 May 1992)

A theoretical estimate for the binding energy of simple isoelectronic acceptors in II-VI semiconductors has been made by means of a numerical variational approximation. The short-range potential associated with an impurity is studied with a method based on the analysis of the crystal ionization energy of the impurity and the host atom it replaces. The lattice relaxation of the host crystal and the electronic polarization of the impurity are also included in the estimates. The estimated results for the isoelectronic substitution in three zinc blendes and four rock salts are compared with some experimental data and found to be in good agreement. The binding mechanism of isoelectronic impurities in II-VI semiconductors is discussed in terms of the short-range impurity potential.

I. INTRODUCTION

It has been known that isoelectronic impurities, the substitutional foreign atoms with the same valence-electron structure as the host atoms they replace, have a profound relation to the optical properties of materials with a wide band gap, due to the formation of the bound excitons.[1–8] In particular, isoelectronic traps have high radiative recombination efficiency and that is the reason for their importance in the study of electroluminescence devices,[9,10] or light-emitting diodes.[11] The mechanism of the bound-exciton formation has been conceived to be as follows:[7] The first carrier is trapped in the uncharged impurity by a non-Coulomb short-range impurity potential and becomes bound to it. The previously neutral impurity then acquires a charge relative to the lattice. The Coulomb field of this charge binds a carrier with the opposite sign, which is localized in a considerably large hydrogenlike orbital. This is called an isoelectronic donor or acceptor, according to the type of hydrogenlike carriers. It has long been a topic of discussion[12] that the sources of contributions to the short-range impurity potential of isoelectronic systems may consist of the difference in the bare core potential, the change in the electronic potential in the vicinity of the impurity, and the strain field resulting from the replacement of the host atom with an impurity, but the subject is still controversial. Experimental evidence made clear that the bound states associated with isoelectronic impurities are quite rare and found only when the impurity atom is either very large, like GaP:Bi (Ref. 13) and InP:Bi (Ref. 5) systems or very small, such as GaP:N (Ref. 14) and ZnTe:O (Ref. 1) systems.

In fact, only large or small atoms can produce the strong impurity potential necessary to bind a free carrier, since they significantly modify the host crystals. Available experimental data[1] indicate that an isoelectronic impurity may bind a hole (an electron) if its electronegativity is smaller (larger) than that of the host atom it replaces. This electronegativity rule for the binding mechanism is instructive but insufficient, since it is not possible to predict those systems that do actually have a bound state.[12] A detailed numerical calculation of the one-electron bound levels for an isoelectronic system of GaP:N has been performed within the framework of the Koster-Slater method by Faulkner.[2] In this treatment, the impurity potential is assumed to be the difference in the atomic pseudopotentials between nitrogen and phosphorus. But the estimated binding energy (~ 1 eV) is much larger than that (~ 20 meV) observed in the experiment. For this discrepancy, Phillips[3] has pointed out that the lattice deformation around the impurity is critical and a bound charged particle polarizes the lattice in such a way as to reduce the binding energy. Allen[4] has proposed a completely different picture of the binding mechanism, in which the spin-orbit coupling or the strain field around the impurity due to the size difference rather than the pseudopotential difference of any two isoelectronic atoms would act as the impurity potential. Baldereschi and Hopfield[6] have proposed a theory for isoelectronic donors by considering the impurity potential as the difference in atomic pseudopotentials, including the spin-orbit coupling, local electronic screening, and lattice relaxation. The theoretical binding energies estimated in this way are generally larger than the experimental values due to the inaccuracy in the atomic pseudopotentials and the matrix elements of impurity potentials on the Wannier functions.

Thus, as revealed in some earlier theoretical works, the binding energies of isoelectronic impurities are very sensitive to the used models, so that the binding mechanism of the carriers is still unclear. In particular, very little theoretical estimating has been done for the binding energies of isoelectronic impurities in II-VI semiconductors, even though some theoretical studies have been performed for the spectrum analysis of bound excitons.[7,8]

Experimentally it was found that isoelectronic impurities such as oxygen, tellurium, and transition-metal ions produce the bound states in some II-VI semiconductors, and their binding energies are larger to a great extent than those observed in III-V semiconductors.[8] An exciton can be bound to oxygen in ZnTe with a binding energy of 0.404 eV,[1] and to tellurium in ZnS and CdS with binding energies of 0.44 and 0.25 eV, respectively.[12]

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Various emission or absorption bands associated with local levels are observed in ZnO:Se, ZnS:Te, CdS:O,[4] and ZnS:O (Ref. 15) systems, even though at present there is no tangible evidence as to whether the centers involved are substitutional or interstitial.

We are concerned with the origin of the potential of isoelectronic impurities forming deep bound excitons in II-VI semiconductors and the estimate of their binding energies. This paper describes the results estimated theoretically for the binding energies of isoelectronic acceptors. The estimate for binding energies of isoelectronic donors will be excluded in this study, since it is difficult to choose the appropriate wave functions for deep holes in the variational approximation, although they could be treated approximately as a hydrogenic $1s$ state[2] or $2p$ state.[16] Furthermore, we will restrict ourselves to the estimate for the binding energies of "simple" isoelectronic acceptors. The term simple stands for the completely filled shell, which is distinguished from the term "structural" for the partly filled d or f shells in transition-metal ions and rare-earth ions.[17]

In Sec. II the model potential for simple isoelectronic acceptors in II-VI semiconductors will be introduced, which consists of the simple square-well potential with a polarization-potential tail. The potential depth of the square well will be determined by an analysis of the crystal ionization energy.

In Sec. III the binding energies of simple isoelectronic acceptors will be calculated in the numerical variational approximation. For the trial functions, the spherical Bessel function in the square-well potential region and the spherical harmonic in the polarization-potential region are chosen.

In Sec. IV the estimated results, variational parameters, and binding energies will be discussed in terms of the potential strength of impurities and the polarization effect and then compared with some observed values.

II. IMPURITY POTENTIALS OF ISOELECTRONIC ACCEPTORS

As mentioned in Sec. I, the isoelectronic impurity potential has been conceived to be non-Coulomb short-range potential occurring as a result of the difference in bare atomic pseudopotentials between the impurity and the host atom, the spin-orbit coupling, and the strain field.

As for our present concern, isoelectronic acceptors in II-VI semiconductors, the spin-orbit coupling, and the strain field would play no role in binding a conduction electron, since the former works at the valence-band edge and the latter is not attractive for an electron in II-VI semiconductors with a nondegenerate conduction-band edge.[4] Thus, the short-range isoelectronic acceptor potential $V_i(\mathbf{r})$ seems to be related to the difference in atomic pseudopotentials of any two isoelectronic atoms.

Within the framework of a one-band, one-site Koster-Slater model, the binding condition of an impurity is[2,6]

$$1+\frac{J}{\langle E\rangle}\leq 0 , \tag{1}$$

where J is the matrix element of $V_i(\mathbf{r})$ on the Wannier functions $\Psi_n(\mathbf{r})$ of the nth band and $\langle E\rangle$ is an average energy over the Brillouin zone of the energy dispersion $\in(\mathbf{k})$. The problem for the impurity located at a lattice site p is simplified considerably in the simplest case of a strong localization at the origin of the coordinates. Then J is written in the well-known form

$$\begin{aligned} J &= \langle \Psi_n(\mathbf{r}-\mathbf{R}_p)|V_i(\mathbf{r})|\Psi_m(\mathbf{r}-\mathbf{R}_q)\rangle \\ &= \delta_{n0}\delta_{m0}\delta_{p0}\delta_{q0}V_{00} , \end{aligned} \tag{2}$$

where V_{00} is a constant representing the magnitude of perturbation. The energy threshold $\langle E\rangle$ in Eq. (1) represents the kinetic part and is defined by

$$\frac{1}{\langle E\rangle}=\frac{\Omega}{(2\pi)^3}\int d^3k\frac{1}{\in(\mathbf{k})} , \tag{3}$$

where Ω is the primitive cell volume.

It should be noted that from Eqs. (2) and (3) the binding condition of an impurity merely stands for a quantum-mechanical fact that bound states exist only if the potential energy J dominates over the kinetic energy $\langle E\rangle$.

The theoretical estimate for the binding energies of isoelectronic impurities based on Eqs. (1), (2), and (3) yields poor results compared with experimental data, especially for II-VI semiconductors, even if the difference in atomic pseudopotentials is used for $V_i(\mathbf{r})$ in Eq. (2).[6]

As Jaros pointed out,[12] the existence of the binding mechanism of deep isoelectronic impurities in II-VI semiconductors may be taken as another sign of the short-range effects in the theory of isoelectronic impurities.

The constant square-well potential V_{00} in Eq. (2), which is generally left undetermined in band-structure calculations, may be evaluated from the experimental values of the average ionization potentials[6] or adjustable potential depth.[2] Indeed, Phillips[18] considered the band-gap difference between any two crystals as the effective square-well depth in the calculation of the binding energy of isoelectronic impurities in III-VI semiconductors. But it is difficult to take into account the difference in the average ionization potentials of II-VI semiconductors as V_{00}, since as a whole they are less than 5 eV (Ref. 19) and would not yield the large binding energy, for instance, 0.404 eV in the ZnTe:O system. We will rely on another way to determine V_{00} based on an analysis of the crystal ionization energy I_c defined by[20]

$$I_c=2U_c+A_b-I_a+Q , \tag{4}$$

where U_c is the cohesive energy of compounds, A_b and I_a the electron affinity of anions and the ionization potential of cations, respectively, and Q is the energy of interaction between the free atom and the crystal environment, about -1 eV. For the highly ionic crystals, U_c is generally expressed by

$$U_c=V_{\mathrm{ma}}-V_{\mathrm{re}} , \tag{5}$$

V_{ma} and V_{re} being the Madelung energy and the Born-Mayer repulsive energy, respectively. The crystal-

ionization energy I_c defined by Eq. (4) is total energy involved in a circular process in which an anion is removed from the crystal, an electron is transported from the anion to the infinitely distant cation previously removed from the host crystal, and these atoms are transported back to their respective lattice sites. Considering that an isoelectronic acceptor is formed in the process where the bonds around an anion are broken, an anion is removed, and an impurity is substituted for it, the potential that the isoelectronic acceptor produces will be given by the difference of the crystal-ionization energy between the anion and the isoelectronic acceptor. Since the cation does not change before and after the substitution of the isoelectronic acceptor, the factor 2 in Eq. (4) is omitted, so that V_{00} is given by

$$\begin{aligned} V_{00} &= I_{ci} - I_c \\ &= (U_{ci} - U_c) + (A_{bi} - A_b) - (I_{ai} - I_a) + (Q_i - Q) \\ &= \Delta U_c + \Delta A_b - \Delta I_a + \Delta Q \ , \end{aligned} \tag{6}$$

where the subindex i denotes the quantities corresponding to isoelectronic acceptors. It should be noted that V_{00} is not an adjustable quantity but a substantial one depending on the host crystal and the impurity, and that it gives an insight into the electronegativity rule, since ΔA_b and ΔI_a have a direct relation to the difference in electronegativity.[21]

Thus the bare square-well impurity potential for isoelectronic acceptors can be evaluated by imposing an appropriate potential-well radius on Eq. (6), as will be discussed in detail in Sec. III. The electronic charge redistribution in the vicinity of the impurity could be taken into account in such a way as to include it in Eq. (6) by using the effective ionic charge. The electronic polarization potential should be included in the short-range potential problems, since it is expected that a free carrier approaching an impurity generates an electronic perturbation that can polarize the lattice in such a manner as to reduce the binding energy.[3]

As a result, the model potential $V_i(\mathbf{r})$ for the binding of isoelectronic acceptors in II-VI semiconductors is written in the form

$$V_i(\mathbf{r}) = -V_0, \quad (r \le r_w) \tag{7a}$$

$$= -\frac{C}{r^4}, \quad (r \ge r_w) \ , \tag{7b}$$

with

$$C = \frac{\alpha_p e^2}{2\epsilon^2} \ , \tag{8}$$

where V_0 is the constant potential with a depth of V_{00}, r_w is the potential-well radius, and α_p and ϵ are the electronic polarizability of the isoelectronic impurity and the dielectric permittivity of the host crystal, respectively.

As for the shape of the potential, this model potential is similar to that of the pseudopotential of the bare ion in the sense that it depends on the potential depth and the model radius.[22] But it is fundamentally different from the pseudopotential, in view of the fact that it is expressed by a substantial potential V_0, and that it varies differently as r^{-4} at long range, depending on a physical quantity C, from the pseudopotential with only the Coulomb potential tail.

III. VARIATIONAL APPROXIMATION

In order to obtain the binding energies of isoelectronic acceptors, the matrix element J of Eq. (2) should be calculated from the model potential of Eqs. (7a) and (7b). In this case, a direct calculation of J on the Wannier functions is very difficult. Moreover, the Schrödinger equation for the polarization potential cannot be solved by any hypergeometric functions.

We will count on a variational approximation to calculate the binding energies of isoelectronic acceptors in which the appropriate trial functions for our model potential are chosen. It should be kept in mind that the model functions for the pseudopotential consist of the spherical Bessel function and the spherical harmonics,[23] and that a simple 1s hydrogenic function can be used as an approximation to the Wannier function.[4] Moreover, the trial function for a rapidly varying discontinuous potential such as the polarization potential of Eq. (7b) would be taken as the approximation of the simple hydrogenic function,[24] even though the asymptotic expansion of the Whittaker function[25] could be used for the numerical estimate of eigenvalues. In this work, we will consider the trial functions Ψ of 1s ground state in the well-known form

$$\Psi_{\rm I} = A j_0(\alpha r) Y_{00} \quad (r \le r_w) \ , \tag{9a}$$

$$\Psi_{\rm II} = B \exp(-\beta r) Y_{00} \quad (r \ge r_w) \ , \tag{9b}$$

where $j_0(\alpha r)$ and Y_{00} are the spherical Bessel function and a spherical harmonic, respectively, α and β the variational parameters, and A and B the normalization constants.

The normalization conditions in each potential region and the condition of the continuity of Ψ'/Ψ at $r = r_w$ give

$$\Psi_{\rm I} = (\alpha^3 \sqrt{8}/\pi)^{1/2} \frac{\sin(\alpha r)}{\alpha r} Y_{00} \quad (r \le r_w) \ , \tag{10a}$$

$$\Psi_{\rm II} = 2\beta^{3/2} \exp(-\beta r) Y_{00} \quad (r \ge r_w) \ , \tag{10b}$$

where

$$\beta = \frac{1}{r_w} - \alpha \cot(\alpha r_w) \ . \tag{11}$$

Then the binding energy E_b of isoelectronic acceptors is given by

$$E_b=\left\langle\Psi\left|-\tfrac{1}{2}\Delta-V_0-\frac{C}{r^4}\right|\Psi\right\rangle$$
$$=\langle\Psi_{\rm I}|-\tfrac{1}{2}\Delta-V_0|\Psi_{\rm I}\rangle+\left\langle\Psi_{\rm II}\left|-\tfrac{1}{2}\Delta-\frac{C}{r^4}\right|\Psi_{\rm II}\right\rangle \quad (12)$$

in atomic units. It should be noted that Eq. (12) will satisfy the binding condition of Eq. (1), i.e., E_b will have negative value when the binding occurs. In Eq. (12) the kinetic-energy part (KE) and the potential energy part (PE) are obtained by integration over the occupied spaces, viz.,

$$\text{KE}=\langle\Psi_{\rm I}|-\tfrac{1}{2}\Delta|\Psi_{\rm I}\rangle+\langle\Psi_{\rm II}|-\tfrac{1}{2}\Delta|\Psi_{\rm II}\rangle$$
$$=\frac{\alpha^2}{\sqrt{2\pi}}[\alpha r_w-\tfrac{1}{2}\sin(\alpha r_w)]+\frac{\beta^2}{2}(1+2\beta r_w-2\beta^2r_w^2)\exp(-2\beta r_w)\,, \quad (13)$$

and

$$\text{PE}=\langle\Psi_{\rm I}|-V_0|\Psi_{\rm I}\rangle+\left\langle\Psi_{\rm II}\left|-\frac{C}{r^4}\right|\Psi_{\rm II}\right\rangle$$
$$=\frac{V_0}{\sqrt{2\pi}}[\sin(2\alpha r_w)-2\alpha r_w]-4C\beta^3\left[\frac{1}{r_w}\exp(-2\beta r_w)+2\beta\left[\ln(2\beta r_w\cdot\gamma)+\sum_{m=1}^{\infty}\frac{(-2\beta r_w)^m}{mm!}\right]\right]. \quad (14)$$

In the integration for the polarization potential, i.e., the last integral term in Eq. (14), we used the integral formula of the integral exponential function[26] in which Euler's constant $\ln\gamma$ is given by 0.5772.

Thus the binding energy of 1s ground state is given as follows, on rearrangement of Eqs. (13) and (14):

$$E_b=\frac{1}{\sqrt{2\pi}}(\alpha^2-2V_0)[\alpha r_w-\tfrac{1}{2}\sin(2\alpha r_w)]+\frac{\beta^2}{2}(1+2\beta r_w-2\beta^2r_w^2)\exp(-2\beta r_w)$$
$$-4C\beta^3\left[\frac{1}{r_w}\exp(-2\beta r_w)+2\beta\left[\ln(2\beta r_w\cdot\gamma)+\sum_{m=1}^{\infty}\frac{(-2\beta r_w)^m}{mm!}\right]\right]. \quad (15)$$

We then have the derivative of E_b for the variational parameter α which can be also expressed as β in terms of Eq. (11):

$$\frac{\partial E_b}{\partial\alpha}=\frac{1}{\sqrt{2\pi}}\{2\alpha[\alpha r_w-\tfrac{1}{2}\sin(2\alpha r_w)]+(\alpha^2-2V_0)[r_w-r_w\cos(2\alpha r_w)]\}$$
$$+\beta\beta'(1+2\beta r_w-6\beta^2r_w^2+2\beta^3r_w^3)\exp(-2\beta r_w)+4C\frac{\beta^2\beta'}{r_w}(3-2\beta r_w)\exp(-2\beta r_w)$$
$$-8C\beta^3\beta'\left[4\ln(2\beta r_w\cdot\gamma)+1+\sum_{m=1}^{\infty}\frac{(-2\beta r_w)^m}{m!}\left[\frac{4}{m}+1\right]\right], \quad (16)$$

where

$$\beta'=\alpha r_w[1+\cot^2(\alpha r_w)]-\cot(\alpha r_w)\,. \quad (17)$$

V_0, C, and r_w in Eqs. (15) and (16), which are quantities to be determined previously for the numerical variational approximation, are evaluated as follows: In Eq. (6) we can put $\Delta I_a=0$ and $\Delta Q=0$, since the substitution of an isoelectronic impurity for an anion has no effect on the change of these quantities. As for ΔU_c, we will count on our previous work,[27] where it is expressed as a sum of the difference of the effective Madelung energy $\Delta V_{\rm ma}$ and the Morse potential $\Delta V_{\rm mo}$ between the impurity and the host it replaces. Keeping in mind that they account for the ionic binding and the covalent binding character of II-VI semiconductors, respectively, we express ΔU_c by

$$\Delta U_c=\Delta V_{\rm ma}+\Delta V_{\rm mo}=NZ^{*2}e^2\left[\frac{1}{r_{0i}}-\frac{1}{r_0}\right]$$
$$+2N\{D_i\exp[-a_{0i}(r_{0i}-r_{ci})]-D\exp[-a_0(r_0-r_c)]\}$$
$$+N\{D_i\exp[-2a_{0i}(r_{0i}-r_{ci})]-D\exp[-2a_0(r_0-r_c)]\}\,, \quad (18)$$

where Z^* is the effective ionic charge accounting for the partially ionic binding character of II-VI semiconductors, r_0 and r_c are the nearest-neighbor distance and the covalent bond length, respectively, and D and a_0 are a bond energy and a constant, respectively. N is the number of bonds per unit cell, i.e., $N=4$ for zinc blendes, whereas $N=6$ for rock salts. The subindex i is used to represent the quantities corresponding to isoelectronic impurities.

$\Delta V_{\rm ma}$, the first term in Eq. (18), is considered to occur as a result of the maximum lattice relaxation of the nearest neighbors, which is a similar expression to that seen in some previous works for II-VI semiconductors.[6,28] The relaxation of the nearest neighbors is expected to be at most equal to the difference between covalent radii of

the impurity atom and the host atom it replaces. The contributions of neighbors farther than the ones nearest to $\Delta V_{\rm ma}$ have not been included, since the range of the lattice relaxation is not clearly defined for them. It is similar to the crystal-field theory to consider the change of the electrostatic potential produced by the nearest surrounding ions.

The introduction of the Morse potential in place of $V_{\rm re}$ in Eq. (5) is based on replacement of the host atom with an impurity, which means cutting the nearest bonds and substituting an impurity without destroying the lattice symmetry around it.

ΔA_b, another quantity consisting of V_0, is replaced by the differential electron affinity $\Delta A_b^{-z^*}$, which is related to Z^* by[27]

$$\Delta A_b^{-z^*} = \frac{Z^*}{2} \Delta A_b \ . \tag{19}$$

$\Delta A_b^{-z^*}$ can be determined easily from the electron affinity of chalcogenide ions, i.e., $O^{2-} = -6.63$, $S^{2-} = -4.03$, $Se^{2-} = -4.4$, and $Te^{2-} = -3.3$ eV.[27]

Table I represents the data on quantities related to ΔU_c. The data were taken from our previous works,[27,29] which are devoted to the estimates for the electronic polarizabilities and the effective ionic charges of II-VI semiconductors. It should be noted that Z^* accounts for the electronic charge redistribution due to the covalent bonding character, so that the covalent bonding effect on the change in the electronic potential in the vicinity of the impurity has already been included in the model potentials of Eqs. (7a) and (7b).

The polarization-potential constant C of Eq. (8) will be easily determined, once the electronic polarizabilities α_p of isoelectronic impurities are known. To our knowledge, there is little data on α_p except for our theoretical results.[27] We will use them for α_p, since they give insight into the electronic polarizabilities of isoelectronic impurities in II-VI semiconductors in the absence of no experimental evidence.

Table II shows the results for V_0 estimated from Eqs. (6), (18), and (19) by using the data in Table I. In the estimate of ΔU_c, the quantities denoted by the subindex i in Eq. (18) were chosen from Table I as values corresponding to chalcogenides produced by impurities, for instance, r_0, r_c, D, and a_0 of ZnO in Table I are chosen for r_{0i}, r_{ci}, D_i, and a_{0i} of ZnS:O system. As shown in Table II, V_0 has positive value only when an impurity smaller in size than the host atom is substituted, whereas it has negative value in the opposite cases. Only one exception appears in the case of the CdS:O system. In addition, the substitution for the host atoms of impurities from farther rows of the Periodic Table yields a larger absolute value of V_0. These tendencies have been seen clearly in the earlier experiments and explained by a theory based on the electronegativity rule[16] but now have a more detailed theoretical background based on crystal-ionization energy.

It is worthwhile noting that the analysis of V_0 showing the negative values in Table II gives insight into the hole binding of isoelectronic donors larger than the host atom in size such as a ZnS:Te system, in view of the fact that it may be one of the potential sources for the hole binding in addition to those mentioned in Secs. I and II.

The potential-well radius r_w is a crucial quantity, since there are no bound states if the potential strength is less than a certain critical value, while the binding energy increases rapidly with it beyond the critical value. Although it is not unique to choose r_w in the strict sense, there are some ways for it, for example, to take the pseudopotential model radius R_M (Ref. 22) chosen at some convenient value greater than the core radius, Wigner-Seitz cell radius,[30] sphere radius R_s (Ref. 22) containing one electron, or simply the covalent radius R_c.[18,31] As shown in Eqs. (6) and (18), the potential-well depth is conceived to originate from the change of the Madelung

TABLE I. Physical properties of II-VI semiconductors, the effective ionic charge Z^*, the nearest-neighbor distance r_0, the covalent bond length r_c, a bond energy D, and a constant a_0 related to the Morse potential. The data are chosen from Refs. 27 and 29. W denotes wurtzites, ZB denotes zinc blendes, and RS denotes rock salts.

Compounds	Z^*	r_0 (Å)	r_c (Å)	D (eV)	a_0 (10^{-8} cm^{-1})
ZnO (W)	1.085	1.970	1.950	2.559	1.875
ZnS (ZB)	1.195	2.342	2.350	1.995	1.511
ZnSe (ZB)	0.955	2.454	2.450	1.821	1.478
ZnTe (ZB)	0.784	2.640	2.630	1.691	1.384
CdO (RS)	0.827	2.348	2.342	0.818	1.845
CdS (ZB)	1.381	2.524	2.570	1.840	1.396
CdSe (ZB)	0.783	2.621	2.630	1.691	1.384
CdTe (ZB)	0.741	2.800	2.810	1.561	1.290
CaO (RS)	1.310	2.405	2.415	0.818	1.877
CaS (RS)	1.212	2.848	2.840	0.614	1.931
CaSe (RS)	0.958	2.955	2.947	0.396	2.272
CaTe (RS)	0.669	3.173	3.145	0.353	2.391
SrO (RS)	1.387	2.580	2.582	0.705	1.938
SrS (RS)	1.283	3.010	3.007	0.600	1.908
SrSe (RS)	1.048	3.115	3.114	0.364	2.230
SrTe (RS)	1.079	3.331	3.312	0.323	1.799

TABLE II. Potential-well depth V_0 resulting from the difference in the effective Madelung potential energy ΔV_{ma}, the Morse potential ΔV_{mo}, and the differential electron affinity ΔA_b^{-z*} between the isoelectronic impurity and the host atom it replaces. All quantities are given in electron volts.

		ΔV_{ma}	ΔV_{mo}	ΔA_b^{-z*}	V_0		ΔV_{ma}	ΔV_{mo}	ΔA_b^{-z*}	V_0
ZnS:	O	6.63	2.22	−1.55	7.30	S				
	Se	−1.60	−0.70	−0.22	−2.52	Te	−3.97	−1.22	0.44	−4.75
ZnSe:	O	5.26	2.92	−1.07	7.11	S	1.02	0.70	0.18	1.90
	Se					Te	−2.46	−0.52	0.53	−2.45
ZnTe:	O	4.56	3.44	−1.31	6.69	S	1.71	1.22	−0.29	2.64
	Se	1.02	0.52	−0.43	1.11	Te				
CdS:	O	3.26	−4.05	−1.80	−2.58	S				
	Se	−1.61	−0.57	−0.26	−2.44	Te	−4.29	−1.09	0.50	−4.88
CaS:	O	8.21	1.22	−1.58	7.85	S				
	Se	−1.61	−1.31	−0.22	−3.15	Te	−4.56	−1.56	0.44	−5.69
CaSe:	O	6.14	2.53	−1.07	7.60	S	1.01	1.31	0.18	2.50
	Se					Te	−1.84	−0.27	0.53	−1.58
SrS:	O	7.87	0.87	−1.67	7.08	S				
	Se	−1.59	−1.17	−0.24	−3.00	Te	−4.55	−1.46	0.47	−5.55
SrSe:	O	6.32	2.04	−1.17	7.19	S	1.06	1.17	0.19	2.43
	Se					Te	−1.98	−0.29	0.58	−1.69

potential due to the lattice relaxation of the nearest neighbors and the Morse potential due to the replacement of the host atom with the impurity. That is the reason why we chose R_c for r_w. For comparison, we have also estimated the binding energies by choosing R_s for r_w. Although R_s of chalcogenide ions (S=1.889, Se=1.993, and Te=2.084 a.u.) (Ref. 22) is almost the same as R_M (S, Se, and Te=2.0 a.u.), the former will be chosen here, since it gives more comparable results than the latter. As for oxygen with no available R_s and R_M, the binding energy will be estimated by using another covalent radius.[32]

IV. RESULTS AND DISCUSSION

The results for the variational parameter α and the resulting binding energies E_b from the numerical calculation of Eqs. (15) and (16) are listed in Tables III and IV. For comparison, the observed binding energies are also listed on the last column. Unfortunately, we have not enough experimental data to compare with our theoretical results except for ZnTe:O and ZnSe:O systems. At present, there is no direct evidence as to whether oxygen incorporated in ZnS acts as isoelectronic acceptor or not. The binding energy of 0.59 eV in ZnS:O systems seen in Table III is observed in the ZnS mixed with a few percent ZnO.[33] It has been known that sulfur is replaced with oxygen at the same normal lattice site in the formation of the solid solution of the ZnS-ZnO system.[15] Moreover, in the recent electron-probe microanalysis,[10] it has been found that oxygen in ZnS thin films acts as a substitutional impurity. Thus, oxygen in ZnS may be one possible isoelectronic impurity. As for II-VI rock salts, there is little experimental data for isoelectronic impurities and it is known only that the oxygen doping in CaS and SrS affects their optical properties to a great extent.[34,35]

As revealed in Tables III and IV, E_b shows the same variation depending on r_w, since it contributes to the determination of α, which is one of the outstanding features in the square-well potential model. Furthermore, it decreases by a considerable amount in the order of O^{2-}, S^{2-}, and Se^{2-}. As for oxygen, E_b (0.45–0.68 eV) obtained from the choice of $R_c=0.73$ Å for r_w is in good agreement with the data of ZnS:O and ZnTe:O systems. The discrepancy seen in the ZnSe:O system is probably attributable to the fact that the experimental value was evaluated within the framework of the effective-mass approximation. It should be noted that, in principle, the effective-mass approximation neglects the short-range potential due to the impurity core and leads to inaccurate results in the system with large localized charges in the region of the short-range potential.[12] The choice of $R_c=0.678$ Å gives $E_b=0.36$–0.93 eV, which are somewhat smaller, but not bad results. From the estimated results, it is suggested that the difference in the crystal ionization energy between the impurity and the host atom may be a source of short-range potentials. Keeping in mind that the change of the effective Madelung energy originating from the lattice relaxation in the range of the covalent bond length predominantly contributes to V_0, one finds that oxygen showing the large difference in the covalent radius as compared with the host atom it replaces is the possible isoelectronic acceptor forming the deep-bound excitons in II-VI semiconductors. But it does not mean that the binding energies of isoelectronic acceptors can be simply estimated by means of the difference of the covalent bond length between the impurity and the host atom it replaces. As shown in Table III, the binding energy of the ZnTe:O system is smaller than those of any other oxygen-related system, irrespective of the largest difference of the bond length (r_0-r_{0i}), as shown in Table I. This is due to the small effective ionic charge of ZnTe, that is to say, the large covalent binding character, which results in the small change of the effective Madelung energy. Moreover, there are no bound states for the electron in the CdS:O system in spite of the difference in the bond

TABLE III. Variational parameter α and the resulting binding energy E_b of isoelectronic oxygen acceptors in II-VI semiconductors depending on the potential-well radius r_w. α_p and ϵ are the electronic polarizability of isoelectronic acceptors and the dielectric permittivity of host crystals, respectively. The values in parentheses represent the results estimated for the oxygen impurity without considering the polarization effect of isoelectronic impurities.

Systems	α_p (Å^3) Ref. 27	ϵ	r_w (Å)	α (Å^{-1})	E_b (eV) this work	E_b (eV) observed
ZnS:O	0.771	8.9[a]	0.678[b]	1.055	0.444	
				(1.058)	(0.537)	
			0.730[c]	1.058	0.564	0.59[d]
				(1.054)	(0.660)	
ZnSe:O	1.096	9.2[a]	0.678[b]	1.040	0.414	
				(1.044)	(0.505)	
			0.730[c]	1.044	0.525	0.08[e]
				(1.041)	(0.621)	
ZnTe:O	0.668	10.4[a]	0.678[b]	1.010	0.335	
				(1.014)	(0.436)	
			0.730[c]	1.012	0.453	0.404[f]
				(1.011)	(0.537)	
CaS:O	0.778	9.3[g]	0.811[b]	1.120	0.932	
				(1.088)	(1.045)	
			0.730[c]	1.098	0.681	
				(1.092)	(0.785)	
CaSe:O	1.337	7.8[g]	0.811[b]	1.085	0.851	
				(1.070)	(0.967)	
			0.730[c]	1.081	0.614	
				(1.075)	(0.726)	
SrS:O	0.824	9.4[g]	0.811[b]	1.045	0.724	
				(1.034)	(0.818)	
			0.730[c]	1.041	0.521	
				(1.039)	(0.613)	
SrSe:O	1.334	8.5[g]	0.811[b]	1.054	0.745	
				(1.042)	(0.850)	
			0.730[c]	1.050	0.535	
				(1.046)	(0.636)	

[a]Y. S. Park and B. K. Shin, in *Electroluminescence*, edited by J. I. Pankove, Topics in Applied Physics, Vol. 17 (Springer-Verlag, Berlin, 1977), p. 133.
[b]Reference 31.
[c]Reference 32.
[d]Reference 15.
[e]Reference 11.
[f]Reference 1.
[g]Reference 38.

length, which is due to the repulsive Morse potential and the large electron affinity shown in Table II. These suggest that the chemical bonding properties act as an important source of impurity-binding potentials. On the other hand, as shown in Table IV, sulfur and selenium show the binding energies in the range 0.07–0.19 eV and 0.02 eV, respectively, depending on the host crystals. The latter is a very small value, in support of the experimental fact that no bound states are observed in the ZnTe:Se system.[36]

The effect of the electronic polarization on the binding of isoelectronic acceptors can be investigated in such a simple way as to use only the square-well potential and estimate the binding energies in the same variational procedure. We estimated the binding energies for the oxygen-related system without the polarization potential. The estimated results are listed in parentheses in Table III. In any case, the variational parameter α shows a bit of change and the binding energies increase by 0.1 eV.

From the estimated results, it is concluded that the difference in effective Madelung energy between the impurity and the host atom due to the lattice relaxation, the difference in the Morse potential due to replacement of the host atom with the impurity, and the difference in the differential electron affinity act as the short-range impurity potential that binds an electron in II-VI semiconductors, while the polarization of impurity plays a role in reducing the binding energy through the spatial variation of the wave functions.

At present, the method used in this work does not seem to apply to estimating the hole binding energies observed in II-VI semiconductors such as ZnS:Te and

TABLE IV. Variational parameter α and the resulting binding energy E_b of isoelectronic sulfur and selenium acceptors in II-VI semiconductors, depending on the potential-well radius r_w. α_p and ϵ are the electronic polarizability of isoelectronic acceptors and the dielectric permittivity of host crystals, respectively.

Systems	α_p (Å^3) Ref. 27	ϵ	r_w (Å)	α (Å^{-1})	E_b (eV) this work	E_b (eV) observed
ZnSe:S	2.133	9.2[a]	1.127[b]	0.530	0.067	
			1.000[c]	0.520	0.044	
ZnTe:S	2.404	10.4[a]	1.127[b]	0.635	0.161	
			1.000[c]	0.630	0.108	
CaSe:S	2.705	7.8[d]	1.236[b]	0.620	0.185	
			1.000[c]	0.610	0.092	
SrSe:S	2.610	8.5[d]	1.236[b]	0.610	0.173	
			1.000[c]	0.600	0.086	
ZnTe:Se	4.397	10.4[a]	1.225[b]	0.390	0.020	
			1.060[c]	0.380	0.012	no bound[e]

[a]Y. S. Park and B. K. Shin, in *Electroluminescence*, edited by J. I. Pankove, Topics in Applied Physics, Vol. 17 (Springer-Verlag, Berlin, 1977), p. 133.
[b]Reference 31.
[c]Reference 22.
[d]Reference 38.
[e]Reference 36.

CdS:Te, even though it gives insight into them in view of the fact that the potential-well depths evaluated by this method for Te in sulfides are large enough to bind a hole deeply, as shown in Table II. As argued in Sec. I, the potential sources for the binding of a hole are conceived to be different from those for an electron due to the degeneracy of the valence bands, which are lifted by the spin-orbit coupling, or to the strain field. The Green-function approach[37] may help to calculate the binding energy of the hole. The lack of evidence for the isoelectronic impurities in II-VI semiconductors makes the mechanism for the formation of deep-bound excitons ambiguous. Indeed, the substitution of an impurity with a large size difference for the host atom causes the free energy of the system to increase in the thermodynamical sense, so that the solubility of the isoelectronic impurity will be extremely low.[36] Moreover, the production of the isoelectronic impurity system in II-VI semiconductors requires the large formation energy to preserve the lattice symmetry around the impurity, since the large electrostatic potential acts on it. Thus it is expected that the formation of the bound excitons is difficult to observe in II-VI semiconductors but, once they are formed, the binding energies will become relatively large.

The bound excitons in II-VI semiconductors attract much attention to investigate the excitation mechanism of the optical devices, for instance, electroluminescence devices.[10] But they will have little chance to exist at high fields of above 10^6 V/cm, since the electron-hole pair bound by the Coulomb potential will be dissociated by the field ionization, even though the electron itself, with a large binding energy of about 0.5 eV can be bound in the impurity. In view of this, if oxygen and tellurium showing large binding energies substitute for an anion within a distance of the carrier pairing, they could form stable bound excitons at high fields, since the deep-bound electron and the deep-bound hole would not suffer the large field ionization. Nevertheless, it could not be ruled out that a certain interaction between the luminescent center and the isoelectronic impurity acts as the source of the outstanding change in the optical properties shown in these devices.[34,35]

V. CONCLUSIONS

The binding energies of isoelectronic acceptors in II-VI semiconductors have been calculated using a simple theory based on the analysis of the short-range impurity potential and a numerical variational approximation. The short-range impurity potential to deeply bind an electron has been analyzed by the crystal-ionization energy consisting of the difference in the effective Madelung energy, the Morse potential, and the differential electron affinity between the impurity and host atom it replaces. In the estimate of the binding energies, the effect of the polarization of the impurity has also been investigated.

The potential-well depth evaluated from the crystal-ionization energy gives a criterion for whether the impurity binds an electron or a hole. Generally, due to the large change of the effective Madelung energy resulting from the lattice relaxation, an impurity smaller in size than the host atom it replaces produces a short-range potential that binds an electron. The chemical potential such as the Morse potential and the differential electron affinity also act as important sources for the short-range impurity potentials, which depend sensitively on the host crystal.

The numerical results for the variational approximation of the binding energies are in satisfactory agreement with some observed values when the covalent radius of the impurity is chosen for the critical radius of the model potential considered. In this case, the binding energy of the oxygen arises in the range 0.45–0.68 eV, whereas

those of sulfur and selenium are in the range 0.07–0.19 and 0.02 eV, respectively. This agreement seems to be due to the fact that the model potential largely depends on the difference in the effective Madelung energy resulting from the lattice relaxation of the nearest neighbors. The electronic polarization of the impurities plays a role in reducing the binding energies to a certain extent through the spatial variation of the wave functions.

From the theoretical results, it is suggested that oxygen in II-VI sulfides and selenides would be an isoelectronic acceptor to bind the deep excitons, whose binding energy is larger than that observed in the ZnTe:O system.

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