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Chemical shift and electron-phonon coupling in polar semiconductors

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The dissociation energy of an exciton-impurity complex and the energies of impurity states are known to depend on the chemical nature of the impurity. In a variety of semiconductors this chemical shift represents itself in the form of linear relations analogous to Haynes' rule. We present an explanation of some of these relations by describing the influence of the special chemical impurity on the state energies in terms of a general chemical-shift potential. In particular, this chemical-shift potential need not be restricted to the central cell. Our concept permits us to compare the results of the bound-polaron theory with experimental data. It is found that the results of the bound-polaron model, which in our view describes an impurity with vanishing chemical-shift potential, are in good accord with experiment.

I. INTRODUCTION

Luminescence in semiconductors takes place mainly through impurity centers to which excitons are bound before they recombine radiatively. In these processes all kinds of impurities can be involved: neutral or ionized donors and acceptors and isoelectronic traps. The existence of exciton-impurity complexes as predicted by Lampert[1] has been verified first by Haynes.[2] In particular, he found for donors and acceptors in Si the linear relation

$$E_{\mathrm{BX}} = 0.1 E_i \tag{1}$$

between the dissociation energy E_{BX} of the complex and the ionization energy E_i of the impurity (Haynes' rule). From subsequent experimental results one can set up the empirical relations

$$E_{\mathrm{BX}} = a_1 + b_1 E_i \tag{2a}$$

for neutral acceptors in III-V compounds[3,4] and

$$E_{\mathrm{BX}} = A' + B'(E_{2p} - E_{1s}) \tag{2b}$$

for neutral and ionized donors in II-VI compounds.[5-7]

In addition to Eqs. (2a) and (2b) the linear relation

$$E_{2p} - E_{2s} = A + B(E_{2p} - E_{1s}) \tag{3}$$

has been found from luminescence data in n-doped CdS,[6] and ZnSe.[7] In these relations E_{1s}, E_{2s}, and E_{2p} are donor-state energies and the constants a_1, b_1, A', B', A, and B depend only on the host crystal, but not on the defect under consideration.

The dependence of bound-exciton and impurity-state energies on the special chemical nature of the impurity (chemical shift) can take on more complex forms[8,9] than given in Eqs. (1)–(3). Nevertheless we restrict our attention to these linear relations, which in spite of their simplicity have not yet found an extensive theoretical explanation.

The state of the art in theory can be characterized as follows: In a first approximation, impurities or exciton-impurity complexes are described by a point-charge model, in which the Coulomb interaction between the charged particles is considered whereas the chemical nature of the impurity is neglected.[10] As for the bound-exciton problem, this simple model has been refined by the inclusion of electron-phonon interaction.[11,12] The impurity model has been developed beyond the effective-mass approximation[13] by studying central-cell corrections,[14-17] long-range strain fields due to size mismatch between the host-lattice and impurity atoms,[17-19] and the influence of electron-phonon coupling (the bound-polaron problem).[20-25]

Theoretical results for the bound-exciton problem[11,12] and for the bound-polaron problem,[20-25] which are obtained by neglecting the chemical shift, cannot be unambiguously compared with experimental data, as the latter naturally contain the influence of the chemical impurity.

The chemical shift has been studied for impurities in Si by Pantelides,[16] who combined pseudopotential theory and effective-mass approximation. These calculations were not pursued towards an explanation of Haynes' rule. Baldereschi[26] has derived the linear relation (2b) by assuming a square-well potential within the central cell of the donor. Such a chemical-shift potential affects only states $|n\rangle$ with appreciable probability Δ_n to find the electron in the central cell.[27] When treating this potential as a perturbation of the point-charge model, the resulting energy corrections are proportional to Δ_n and differ from zero only for s-symmetric states. This model allows one to explain Eq. (3) and yields $B = \Delta_{2s}/\Delta_{1s} = \frac{1}{8}$, whereas the experimental values are $B = 1/4.46$ for CdS,[6] and $B = 1/4.94$ for ZnSe.[7] This discrepancy indicates that the square-well central-cell potential does not correctly describe the chemical shift in systems like ZnSe and CdS. In addition, it is the relatively large $2p$-$2s$ splitting in these materials[6,7] which makes us suspect that the impurity potential might contain a "Lamb-shift potential." In polar semiconductors the origin of such a potential is the electron-phonon interaction.[20–25]

In Sec. II of the present paper we use the experimental result of Eq. (2a) and derive the linear relations (2b) and (3) by assuming a chemical-shift potential, which is not restricted to the central cell. In Sec. III we discuss the influence of the electron-phonon interaction on bound-exciton and impurity states and draw some conclusions on the nature of the chemical-shift potentials in CdS and ZnSe. The results of this paper are summarized in Sec. IV.

II. CHEMICAL-SHIFT POTENTIAL

For studying the chemical shift of the energies of impurity and bound-exciton states we distinguish between two contributions to the energy eigenvalues: The first is determined by host crystal parameters and is therefore independent of the special chemical impurity (this contribution is designated by the index 0) and the second, the chemical-shift energy, depends on the special chemical nature of the defect (denoted by cs). Thus we write

$$E_i = E_i^0 + E_i^{\text{cs}} \tag{4}$$

for the ionization energy of the impurity and

$$E_{\text{BX}} = E_{\text{BX}}^0 + E_{\text{BX}}^{\text{cs}} \tag{5}$$

for the dissociation energy of an exciton-impurity complex. Using Eq. (4) we can rewrite Eq. (2a) as

$$E_{\text{BX}} = a_1 + b_1 E_i^0 + b_1 E_i^{\text{cs}} \tag{6}$$

and obtain by comparison with Eq. (5) the relations

$$E_{\text{BX}}^0 = a_1 + b_1 E_i^0 \tag{7}$$

and

$$E_{\text{BX}}^{\text{cs}} = b_1 E_i^{\text{cs}} \; . \tag{8}$$

Equation (7) connects quantities, which are determined by the host crystal, while Eq. (8) correlates the chemical-shift energy of the bound-exciton state with that of the impurity state: The ratio between the chemical-shift energies $E_{\text{BX}}^{\text{cs}}$ and E_i^{cs} for different impurities is a constant, which is characteristic for the host crystal, but does not depend on the chemical nature of the impurities involved (e.g., this ratio is the same for all neutral donors in[7] ZnSe). This can be understood if the chemical-shift energies E_i^{cs} and $E_{\text{BX}}^{\text{cs}}$ depend linearly on one and the same chemical-shift parameter p_{cs}, which characterizes all the influence of the chemical nature of the defect on these energies. Thus they can be written

$$E_i^{\text{cs}} = p_{\text{cs}} Q_i$$

and (9)

$$E_{\text{BX}}^{\text{cs}} = p_{\text{cs}} Q_{\text{BX}} \; ,$$

where Q_i and Q_{BX} do not depend on the chemical nature of the defect but are determined by the host crystal only.

In the following we restrict ourselves to systems like[6] CdS and[7] ZnSe where Eqs. (2b) and (3) are valid. In these materials the chemical-shift energy is small compared to the ground-state energy of the exciton-donor complex or of the donor. [For the bound-exciton system this becomes apparent only if we remember the fact that $E_{\text{BX}}^{\text{cs}}$ in Eq. (5) must be compared to the ground-state energy of the complex, whereas E_{BX} is the difference of this ground-state energy and the binding energy of the free exciton.] It is the smallness of the chemical-shift energy that allows us to interpret E^{cs} in Eqs. (4) and (5) as a first-order energy correction to the energy E^0. Accordingly, the Hamiltonians of the impurity and of the bound-exciton problem are of the form

$$\underline{H} = \underline{H}^0 + \underline{W}^{\text{cs}} \; , \tag{10}$$

where because of Eq. (9) the chemical-shift potential operator $\underline{W}^{\text{cs}}$ must have the form

$$\underline{W}^{\text{cs}} = p_{\text{cs}} \underline{\tilde{W}} \; . \tag{11}$$

$\underline{\tilde{W}}$ is a general potential operator, which reflects host crystal properties and which does not depend on the chemical nature of the defect.

A chemical-shift potential $\underline{W}^{\text{cs}}$ as in Eq. (10) has been used already by Hale[28] to describe the chemical shift of donor ground-state energies in Si and Ge. The chemical-shift potential of Balderes-chi[26] is of the form given in Eq. (11), but was assumed to be a square-well potential in the central cell of the donor. In contrast, our ansatz does not need this restriction, thus a chemical-shift potential may contain long-range terms as well.

We are now able to derive Eqs. (2b) and (3). For this purpose we write down the binding energy of the exciton-donor complex and the energies of the $1s$, $2s$, and $2p$ donor states:

$$\begin{aligned} E_{\text{BX}} &= E_{\text{BX}}^0 + p_{\text{cs}} \tilde{W}_{\text{BX}} \; , \\ E_{1s} &= E_{1s}^0 + p_{\text{cs}} \tilde{W}_{1s} \; , \\ E_{2s} &= E_{2s}^0 + p_{\text{cs}} \tilde{W}_{2s} \; , \\ E_{2p} &= E_{2p}^0 + p_{\text{cs}} \tilde{W}_{2p} \; . \end{aligned} \tag{12}$$

E_n^0 is the energy eigenvalue of $\underline{H}^0$ (Eq. 10) in the state $|n\rangle$ and $p_{\text{cs}} \tilde{W}_n$ is the first-order perturbation correction obtained from the chemical-shift potential, Eq. (11), with the eigenstate $|n\rangle$ of $\underline{H}^0$. Elimination of p_{cs} from Eqs. (12) yields the linear re-

TABLE I. Input data for the bound-polaron model.

	m_e^*/m_0	ϵ_0	ϵ_∞	$\hbar\omega_{LO}$	E_B	R	α
ZnSe	0.16 ± 0.01[a]	8.66[b]	5.75[b]	31 meV[c]	29.1 meV	0.94	0.49
CdS	0.18 ± 0.01[d]	8.67[e]	5.27[f]	38 meV[c]	32.6 meV	0.86	0.60

[a] See Ref. 7.

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lations

$$E_{BX} = A' + B'(E_{2p} - E_{1s}) \tag{2b}$$

and

$$E_{2p} - E_{2s} = A + B(E_{2p} - E_{1s}), \tag{3}$$

where according to the definition of E_n^0 and $\tilde{W}_n$ the constants

$$A = E_{2p}^0 - E_{2s}^0 - B(E_{2p}^0 - E_{1s}^0), \tag{13a}$$

$$B = (\tilde{W}_{2p} - \tilde{W}_{2s})/(\tilde{W}_{2p} - \tilde{W}_{1s}), \tag{13b}$$

$$A' = E_{BX}^0 - B'(E_{2p}^0 - E_{1s}^0), \tag{13c}$$

and

$$B' = \tilde{W}_{BX}/(\tilde{W}_{1s} - \tilde{W}_{2p}). \tag{13d}$$

do not depend on the chemical nature of the impurity

Equation (13a) can be used to check theoretical values for E_n^0 since A and B, as well as A', B' in Eq. (13c) can be determined from experiment. Once the values of E_n^0 are ascertained, Eq. (13c) can be used to define the experimental value of the binding energy E_{BX}^0, by which an exciton is bound to a hypothetical impurity with vanishing chemical-shift energy. This has been done in Ref. 29.

III. INFLUENCE OF ELECTRON-PHONON COUPLING

Before drawing any conclusions on the general chemical-shift potential of Eq. (11) it is necessary to study the eigenvalue problem of $\underline{H}^0$ for the impurity and the exciton-impurity complex, using a hypothetical impurity for which the chemical-shift parameter p_{cs} is zero. Such an impurity is but a special case of the impurities discussed in Sec. II, which means that the resulting eigenvalues of $\underline{H}^0$ must fit into the linear relations (2b) and (3).

Let us discuss first the impurity problem. The hydrogen model (HM)[13] has the eigenvalues

$$E_n = E_{gap} - E_B/n^2; \qquad E_B = m_e^* e^4/2\epsilon_0^2\hbar^2,$$

and does not show any $2s$-$2p$ splitting. In the bound-polaron model (PM), however, this splitting exists as a consequence of the interaction of the impurity electron with the longitudinal-optical phonons.[20-25] As for the bound-polaron theory we refer to the work of Engineer and Tzoar.[24] These authors treat the electron-phonon interaction as a perturbation of the hydrogen problem and compute the energy corrections for the $1s$, $2s$, and $2p$ states to second order in the electron-phonon coupling constant α and for arbitrary values of the electron-impurity coupling constant $R = E_B/\hbar\omega_{LO}$.

We use the results of Engineer and Tzoar[24] to compute the correction of the $2p$-$1s$ and $2p$-$2s$ splitting due to electron-phonon interaction. Since in Ref. 24 results are given only for $R \leq 0.8$ we made (i) an extrapolation with a fifth-order polynomial (PM$_1$) and (ii) a linear extrapolation (PM$_2$). The values that have been obtained by using the input parameters of Table I are given in Table II together with those for the hydrogen model. These results are presented together with the experimental data in Fig. 1 for CdS and Fig. 2 for ZnSe, where the results from the two different extrapolations define the vertical and horizontal error bars at $p_{cs} = 0$. From Figs. 1 and 2 the following conclusions can be drawn.

The hydrogen model does not fit into the linear relation (3). The bound-polaron model of Engineer and Tzoar describes an impurity without chemical shift and yields eigenvalues that fit into the linear relation of the experimental data. Any potential

TABLE II. $2p$-$1s$ and $2p$-$2s$ splitting of the impurity states for the hydrogen model (HM) and the bound-polaron model with polynomial extrapolation (PM$_1$) and linear extrapolation (PM$_2$). All energies in meV.

	$E_{2p}^0 - E_{1s}^0$			$E_{2p}^0 - E_{2s}^0$		
	HM	PM$_1$	PM$_2$	HM	PM$_1$	PM$_2$
ZnSe	21.75	23.05	23.13	0.	1.19	0.97
CdS	24.3	26.34	26.26	0.	0.98	0.94

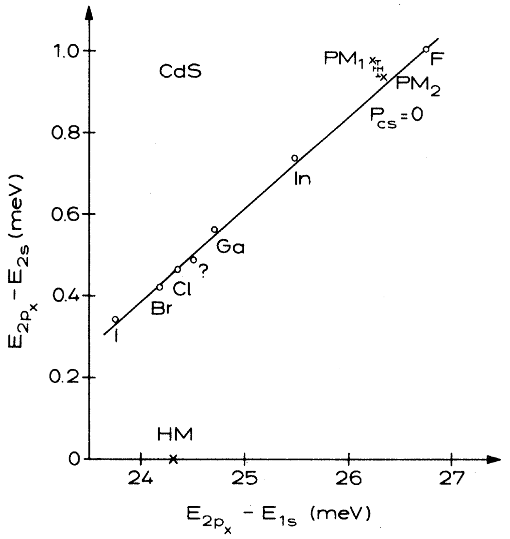

FIG. 1. Experimental (○) and theoretical (×) values for $E_{2p_x}-E_{2s}$ vs $E_{2p_x}-E_{1s}$ in CdS. The experimental values are taken from Ref. 6, the theoretical values are calculated from the hydrogen model (HM) and the bound-polaron model (PM_1, PM_2) and the input data of Table I.

besides Coulomb and electron-phonon interaction, which would contribute significantly to $\underline{H}_i^0$, is restricted by the condition that it can merely shift the point with $p_{cs}=0$ along the straight lines of Figs. 1 and 2. It is unlikely that such a potential really exists.

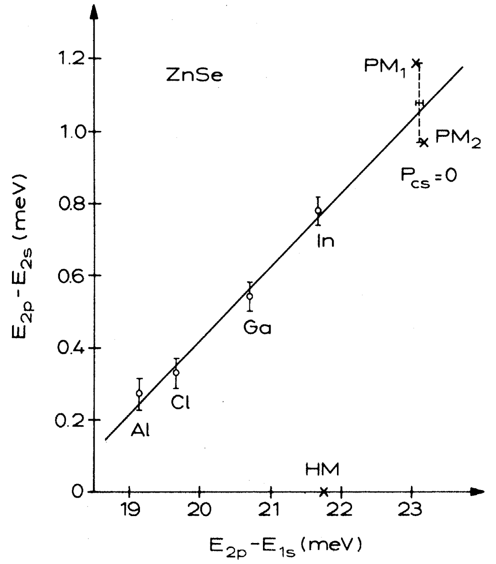

FIG. 2. Experimental (○) and theoretical (×) values for $E_{2p}-E_{2s}$ vs $E_{2p}-E_{1s}$ in ZnSe. The experimental values are taken from Ref. 7, the theoretical values are calculated from the hydrogen model (HM) and the bound-polaron model (PM_1, PM_2) and the input data of Table I.

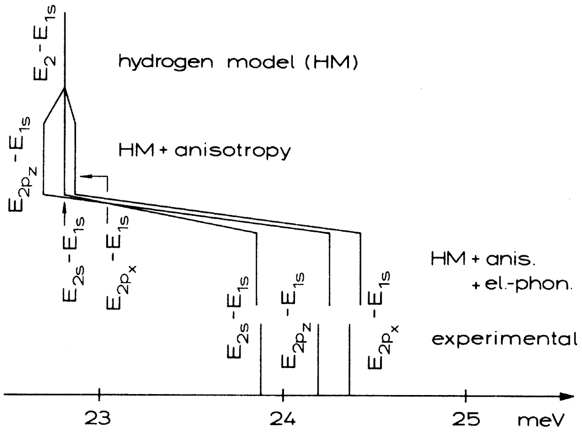

FIG. 3. Effect of anisotropy splitting and electron-phonon coupling on the impurity states of CdS : Cl. The experimental data are taken from Ref. 31.

The influence of electron-phonon interaction on impurity states is seen in another example. In an anisotropic material like CdS, the $2p$ states are not totally degenerate. Due to the anisotropy splitting by the hexagonal crystal field, the terms should order according to $E_{2p_z}<E_{2s}<E_{2p_x}$,[30,31] cf. Fig. 3. From experimental investigations for CdS: Cl it is known, however, that the term order is $E_{2s}<E_{2p_z}<E_{2p_x}$.[32] This contradiction can be explained by considering, besides the anisotropy splitting, the corrections to the impurity states due to electron-phonon coupling (Fig. 3), which is larger for the $2s$ than for $2p$ states.[24]

For the bound-exciton problem it has been already confirmed[11] that electron-phonon interaction must be considered for polar semiconductors. The calculations of Ref. 11 do not consider chemical shift and represent therefore values of E_{BX}^0, i.e., of the binding energy by which an exciton is bound to a hypothetical impurity with vanishing

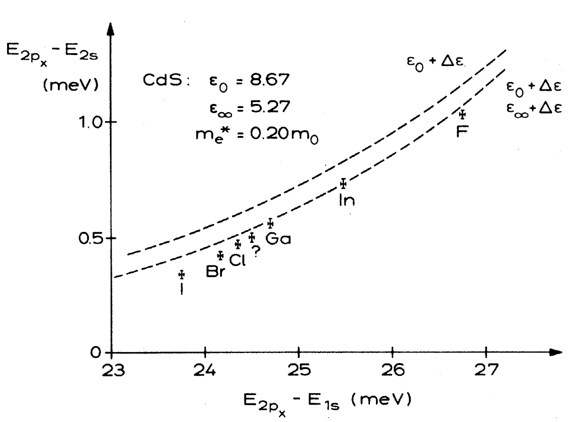

FIG. 4. $E_{2p_x}-E_{2s}$ vs $E_{2p_x}-E_{1s}$ in CdS for different sets of input data. See text.

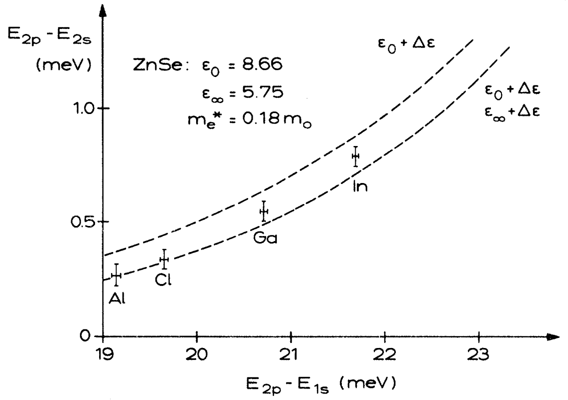

FIG. 5. $E_{2p}-E_{2s}$ vs $E_{2p}-E_{1s}$ in ZnSe for different sets of input data. See text.

chemical-shift potential ($p_{cs}=0$). The corresponding experimental values of E^0_{BX}, to which these results must be compared, are defined by Eq. (13c), where A' and B' can be obtained experimentally and E^0_{2p} and E^0_{1s} are bound-polaron energies.[29]

For the evaluation of the bound-polaron model we used the input data from Table I. Experimental data for m_e^*, ϵ_0, ϵ_∞, and ω_{LO} taken from sources other than cited in Table I in some cases deviate considerably from these values. As we obtain different values for the $2p$-$2s$ and $2p$-$1s$ splitting when starting from different sets of input data, we have to check whether or not the agreement between the polaron data and the experimental results (Figs. 1 and 2) is fortuitous. Therefore, we computed the bound-polaron data for the following cases: (i) for fixed values of m_e^* and ϵ_∞, the value of ϵ_0 was changed; (ii) for fixed values of m_e^*, ϵ_0 and ϵ_∞ were changed by the same amount; and (iii) for fixed values of ϵ_0 and ϵ_∞ the mass value m_e^* was varied.

Figures 4 and 5 contain the graphical representation of these results. Any reasonable data set which is used in the polaron model results in points that are found between the dashed lines. Upper and lower bounds of this area correspond to cases (i) and (ii), respectively, where mass values $m_e^* = 0.18 m_0$ for ZnSe and $0.20 m_0$ for CdS have been used. Corresponding lines with smaller mass values lie within the area between the dashed lines. Therefore, our conclusion that the bound-polaron model describes a hypothetical impurity with $p_{cs} = 0$ in good agreement with experiment, is valid in spite of the uncertainty of the input data.

IV. SUMMARY AND CONCLUSIONS

It has been shown that the linear relations, Eqs. (2b) and (3), can be explained by assuming general chemical-shift potentials, which, in particular, need not necessarily be of short range. We can define an impurity for which the chemical-shift potential is zero and find that this hypothetical impurity is well described by the bound-polaron theory. This has to be the point of reference for any analysis of chemical shift. It is also possible to define the experimental value of the binding energy E^0_{BX} by which an exciton is bound to such an impurity.

In addition, the results of Figs. 4 and 5 may throw some light upon the nature of the chemical-shift potential in CdS and ZnSe. The polaron model results for different sets of input data agree fairly well with the experimental data. Therefore, one might suppose that the influence of the chemical impurity results in a deviation of one (or more) of the parameters ϵ_0, ϵ_∞, m_e^* from their bulk values. The chemical impurity changes the local charge distribution, and thus leads to a variation of the dielectric properties in the vicinity of the impurity. As we are dealing with localized states this variation can be described in a phenomenological way by changing ϵ_0 and ϵ_∞. This change is specific for each impurity and modifies the electron-impurity coupling, which is responsible mainly for the $2p$-$1s$ splitting, and the electron-phonon coupling, which primarily determines the $2p$-$2s$ splitting. This phenomenological explanation of chemical shift in ZnSe and CdS is beyond the perturbational treatment of the chemical-shift potential in Sec. II. It yields a better explanation of the slopes in Figs. 4 and 5 than the central-cell potential of Balderes-chi.[26]

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