

CENTRAL CELL EFFECTS IN THE SHALLOW ACCEPTOR SPECTRA OF Si AND Ge

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The energies of the even-parity excited states of B, Al, Ga and In acceptors in Si have been determined from bound exciton two-hole photoluminescence spectra. Using a semi-empirical short-range potential which is adjusted in each case to give the observed ground state binding energy, calculations of the excited states have been performed. The observed binding energies are in good agreement with the calculated levels of the even parity s-like states. We also use recently introduced analytical *ab-initio* pseudopotentials to represent the impurity potentials and we find that they account for a large part of the observed central cell effects.

I. Introduction

Previously [1], we have studied the odd-parity excited states of group III impurities in Si and Ge using the effective-mass Hamiltonian for degenerate bands and treating the impurity ion as a screened point-charge potential and, an excellent interpretation of the observed data was obtained. More recently [2], we have shown that it is also possible to obtain simple analytical expressions for the most relevant acceptor states as a function of the valence band masses and of the split-off energy, which are valid for all cubic semiconductors. It is well known, however, that the ground state binding energies of shallow acceptors in Si show a strong impurity dependence. We have also seen that this is the case for some of the excited states of various acceptors in Si [3]. In this paper, we use an additional, semi-empirical short-range potential to describe the impurity dependence of the acceptor spectra in Si and Ge. We also apply recently [4] introduced analytical *ab-initio* pseudopotentials to represent the impurity potentials and find that they account for most of the observed central cell effects.

II. Method and results

In this paper, the previously used [1] effective mass approximation (EMA) Hamiltonian, which includes the *q*-dependent screening and the coupling with the split-off valence band, is improved by adding a short-range potential $V_{sr}(r)$ which allows us to distinguish between the different acceptors

$$H = H_{kin} + V_{spc} + V_{sr} . \quad (1)$$

In eq. (1) H_{kin} describes the dispersion of the valence bands, including the split-off band [3] and depends on the parameters γ_1 , μ , δ and Δ whose values for Si and Ge are those given in ref. [5] The screened point charge potential has the simple form

$$V_{spc} = \frac{2[1 + (\epsilon_0 - 1)e^{-\alpha r}]}{r} \quad (2)$$

where $\epsilon_0 = 11.4$ and 15.36 for Si and Ge respectively, and the value of $\alpha = 0.93$ a.u. for both hosts has been obtained from a fit to the numerical $\epsilon(q)$ calculated by Walter and Cohen [6] using a simple expression [1] for $\epsilon(q)$. The short-range potential $V_{sr}(r)$ accounts for differences in the electronic structure of the ionic cores of the various acceptors, as well as for differences in the lattice relaxation around them. In view of the inherent difficulties in constructing this potential from first principle, we adopt first a phenomenological approach and assume $V_{sr}(r)$ to be of the form

$$V_{sr}(r) = \frac{2(\epsilon_0 - 1)(e^{-\alpha r} - e^{-\alpha' r})}{r} \quad (3)$$

where α' is selected for each impurity so that (1) reproduces the observed ground state binding energy. The ground state binding energies in Si are somewhat definition dependent [3]. We have chosen to define the ground state binding energy as the sum of the calculated $2\Gamma_6^-$ binding energy, 3.67 meV, and the observed transition energy from the ground state to the $2\Gamma_6^-$ excited state given by the line 6 in the notation of ref. [7]. This problem does not arise for Ge, since the odd parity excited state spectra of all the acceptors in Ge are virtually identical and agree almost exactly with the calculated spectrum. In Table I we list the values of α' obtained in this manner along with the acceptor state binding energies.

The EMA Hamiltonian (1) gives the correct ground state binding energy for the isocoric Ga acceptors in Ge with the short-range potential set to zero. To correct the small discrepancy between the ground state binding energy calculated for Si without a short-range potential and the measured binding energy of the isocoric Al acceptor in Si, a non-zero short-range potential must be used in (1). We notice, however, that in Si the acceptor ground state binding energy is very sensitive to the values of the function $\epsilon(q)$ and that this function is not known with high accuracy at $q \neq 0$. If somewhat higher values of $\epsilon(q)$ than those used in the present work are more appropriate for Si, the isocoric Al acceptor in Si could be described with a weaker or even vanishing short-range potential in closer analogy with the case of Ge:Ga.

The calculated values of α' given in Table I show in both Si and Ge a very regular trend which is related to the trend in the tetrahedral electronegativities [8] of group III atoms, also reported in the same table. This correlation is based on the fact that both the difference in the short-range potential between two group III acceptors and the difference in electronegativity between two isovalent atoms, mostly come from differences in the electronic structure of the ionic core. In particular, a strongly electronegative acceptor will be described by a short-range potential which is repulsive to holes, i.e. α' much larger than α in (3). Another important feature of the values given in Table I is that for any

Table I. Ground state binding energies E_0 , and the calculated values of α' for the group III acceptors in Si and Ge. The last line refers to the electronegativity of group III atoms in tetrahedrally coordinated environments

		B	Al	Ga	In	Tl
Si	E_0 (meV)	45.83	70.42	74.16	156.94	247.67
	α' (a.u.)	3.00	1.01	0.93	0.73	0.63
Ge	E_0 (meV)	10.8	11.14	11.30	11.99	13.43
	α' (a.u.)	3.00	1.10	0.93	0.70	0.57
Electronegativity		2.00	1.18	1.13	0.99	0.94

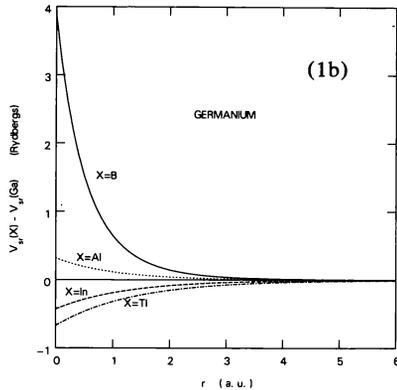
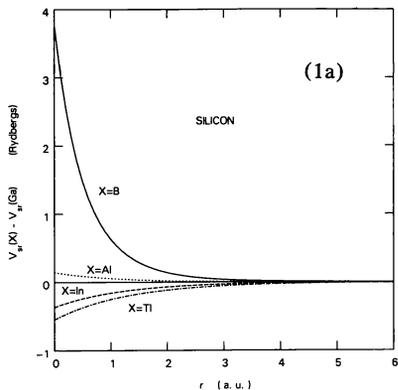


Fig. 1. The short-range potentials for the various impurities in Si (a) and Ge (b) with respect to that of the Ga impurity

given acceptor the value of α' is about the same in Si and in Ge. The quasi-transferability of our short-range potentials from Si to Ge is more clearly illustrated in Fig.1 where we represent the resulting V_{sr} for the B, Al, In and Tl acceptors in Si and Ge with respect to the Ga acceptor. These results clearly indicate that the short-range part of the impurity potential is more related to the atomic properties of the impurity than to the properties of the host lattice. In particular, lattice relaxation around the impurity does not seem to contribute appreciably to V_{sr} because if this were the case, considering that Ge has a 20% softer lattice than Si, a given acceptor would have quite a different short-range potential in Si and Ge, contrary to the results of Fig. 1.

The binding energies of the odd-parity excited states for both Si and Ge calculated from (1) are completely independent of the short-range potential for the values of α' listed in Table I, in agreement with the experimental data, for Ge, and, considering phonon corrections, also for Si [3]. For Ge, the lowest even-parity excited state of the group III acceptors, $2\Gamma_8^+$ has been observed both by submillimeter photoconductivity [9] and by infrared absorption [10], and is in excellent agreement with our calculations. For Si, several even-parity excited states have been observed, as shown in Table II. In Fig. 2 , the first 9 even-parity excited states for acceptors in Si are shown as a function of

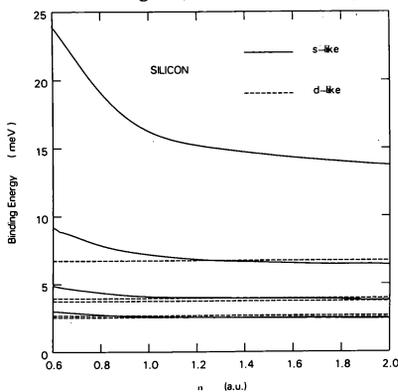


Fig 2. Binding energies of the 9 lowest even parity acceptor excited states in Si as a function of the parameter α' (as defined in eq. (3))

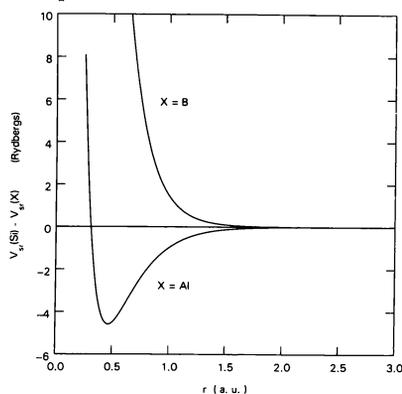


Fig. 3. Short-range components of the ionic pseudopotentials of B and Al referred to Si

α' . Our results predict that only those states with predominantly s-like character reveal pronounced chemical shifts, while the energies of states having predominantly d-like or higher character are not affected by $V_{sr}(r)$. As a result, the ordering of the even-parity excited states changes in going from B to Tl. Due to the symmetry of the bound exciton ground state wavefunctions, the bound exciton two-hole transitions reveal only the predominantly s-like even-parity excited states. In Table II we compare the observed binding energies to the calculated ones corresponding to states with predominantly s-like character, and the agreement is quite good.

Table II. Calculated and measured values of the binding energies of the predominantly s-like even-parity states of B, Al, Ga and In in Si (meV)

B		Al		Ga		In	
calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
13.41	13.44±0.1	16.14	—	16.94	—	20.65	19.22±0.5
6.36	6.38±0.1	7.14	6.11±0.3	7.34	6.58±0.15	8.26	8.12±0.3
3.70	3.85±0.15	4.06	3.78±0.15	4.14	4.02±0.15	4.52	4.48±0.3
2.41	2.7±0.2	2.6	2.6±0.2	2.62	2.78±0.2	2.82	2.59±0.3

The above semiempirical approach has shown that the central cell effects can be explained using short-range potentials that depend mainly on core properties. Recently [4], new ab-initio ionic pseudopotentials, which are analytical and accurately describe several atomic and crystal properties, have been introduced. We have used these pseudopotentials to construct the impurity potentials in order to see if they explain the observed central cell effects. In Fig. 3, we show the differences between the short-range part of the pseudopotentials of Si and B or Al. It is clear that for B the potential is repulsive while for Al the potential is weaker and has both attractive and repulsive components. Preliminary calculations give a binding energy of 38 meV for B and 61 meV for Al, thus showing that most of the observed central cell effects can be explained in terms of these potentials.

- 1) N.O. Lipari and A. Baldereschi: Sol. State Commun. 25 (1978) 665.
- 2) N.O. Lipari: to be published.
- 3) N.O. Lipari, A. Baldereschi and M.L.W Thewalt: Sol. State Commun. 33 (1980) 277.
- 4) W. Andreoni, A. Baldereschi, N.O. Lipari and F. Meloni: to be published.
- 5) J. Bernholc and S.T. Pantelides: Phys. Rev. B15(1977) 4935.
- 6) J.P. Walter and M.L. Cohen: Phys. Rev. B2 (1970) 1821.
- 7) A. Onton, P. Fisher and A.K. Ramdas: Phys. Rev. 163 (1967) 686.
- 8) J. C. Phillips: Bonds and bands in semiconductors (Academic Press, N.Y.) (1973) p.54.
- 9) E.M. Gershenson, G.N. Goltsman and M.L. Kagane: Zh. Eksp. Teor. Fiz 72 (1977) 1466.
- 10) R.L. Jones and P. Fisher: J. Phys. Chem. Solids 26 (1965) 1125.