

# Energy levels of Se and its complexes in Ge

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A Green's function method is used to calculate the energy levels of Se and of its complexes in Ge. The results are compared with experimental data. Some specific models are proposed for impurity centers corresponding to donor levels in Ge:Se.

A selenium impurity atom in germanium has generally been believed to be a doubly charged donor with levels 0.14 and 0.28 eV away from the bottom of the conduction band.<sup>1</sup> Some experiments<sup>2</sup> on the doping of Ge through bombardment with thermal neutrons show, however, that the resulting Se atoms are singly charged centers at lattice sites, and they give rise to a single level in the Ge band gap with an ionization energy of 0.28 eV. The level of 0.14 eV may correspond to either a complex including selenium or a selenium atom in an interstitial position.<sup>2</sup>

In this letter we calculate the local levels of Se and its complexes in Ge, and we find the theoretical position of the level of a single substitutional Se atom. We propose a possible model for a composite center which includes Se and which would be responsible for the level at 0.14 eV. The calculations are based on a semi-empirical version of the Green's function method.<sup>3</sup>

We consider here the cases in which the substitutional Se is at a lattice site, in which there are substitutional selenium atoms at two neighboring sites (Se + Se), and in which a selenium atom forms a complex with a neighboring vacancy (Se + V) in Ge. By analogy with Ref. 3, we find the local levels by solving the basic equation of the Green's function method:

$$\det \|\tilde{I} - \tilde{G}^0 \tilde{U}\| = 0, \quad (1)$$

where  $\tilde{G}^0$  and  $\tilde{U}$  are respectively the submatrix of the Green's function of an ideal crystal and the matrix representing the perturbation operator. The matrix  $G^0$  is constructed on the basis of data<sup>4</sup> on the band structure of germanium calculated by the method of linear combinations of atomic orbitals (in a basis of equivalent orbitals<sup>5</sup>); the interactions of atoms out to the third nearest neighbors are taken into account. The matrix of the perturbation potential is represented as the difference between two matrices:  $\tilde{U} = \tilde{H} - \tilde{H}^0$ , where  $H$  is the Hamiltonian of the crystal with the defect, and  $H^0$  is the Hamiltonian of the ideal crystal. The single-center matrix elements of  $\tilde{H}$  and  $\tilde{H}^0$  (Coulomb integrals) are assumed to be the atomic levels (and are found from data on atomic spectra<sup>5</sup>) in the calculation of  $\tilde{G}^0$  and  $\tilde{U}$ . The two-center matrix elements for the interactions of the atoms of the host crystal are found by a fit to the band structure of the ideal germanium crystal. The two-center matrix elements (resonant integrals) for the Ge-Se interactions are taken to be the same as the corresponding matrix elements for Ge-Ge interactions (since the atomic wave functions of Ge and Se are similar). In this model of a Se impurity at a Ge lattice site, the matrix elements of the perturbation potential are determined entirely by the difference between Coulomb integrals (atomic

levels) for the impurity and host atoms, while the perturbation matrix is an  $8 \times 8$  matrix of type (12) in Ref. 3. The solution of Eq. (1) for Se in Ge then gives us a single level in the band gap of germanium, at  $E_c - 0.32$  eV.

The Se + Se and Se + V complexes in Ge are analyzed by the following approach. The matrix of the perturbation potential  $\bar{U}$  for the Se + Se defect is constructed by analogy with the case of a single Se defect, but for a broader region, including the second coordination sphere of the defect, in a basis of 32 equivalent orbitals (a  $32 \times 32$  matrix). In the case of the Se + V defect, the vacancy is modeled by a "pseudoimpurity" which has vanishing Coulomb and resonant integrals. For the Se site, the Coulomb integrals are chosen in the form of the atomic levels of selenium, as before. The solution of Eq. (1) yields a single level in each of the two cases:  $E_c - 0.22$  eV for the Se + Se defect and  $E_c - 0.13$  eV for the Se + V defect.

In summary, and in agreement with Ref. 2, the results of these calculations show that Se at a lattice site in Ge gives rise to a single local level with an energy  $\sim (E_c - 0.3)$  eV, while Se + Se and Se + V complexes each produce a shallower level; i.e., when we go from the point defect (at a lattice site) to complexes, we find that the local level shifts toward the edge of the conduction band. These calculations show that the level of 0.14 eV can be linked with a Se + V defect complex.

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<sup>2</sup>Yu. A. Osip'yan, V. M. Prokopenko, and V. I. Tal'yanskii, *Pis'ma Zh. Eksp. Teor. Fiz.* **39**, 126 (1984) [*JETP Lett.* **39**, 149 (1984)]; *Zh. Eksp. Teor. Fiz.* **87**, 269 (1984) [*Sov. Phys. JETP* **60**, 156 (1984)].

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<sup>5</sup>A. A. Levin, *Vvedenie v kvantovuyu khimiyu tverdogo tela (Introduction to the Quantum Chemistry of the Solid State)*, Khimiya, Moscow, 1974, p. 256.

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