Electronic structure of the Ge and Se vacancies in GeSe layered semiconductor

Zakir JAHANGIRLI

*Institute of Physics, Azerbaijan National Academy of Sciences, H. Cavid Avenue,
33, Az-1143, Baku-AZERBAIJAN
e-mail: cahanzakir@yahoo.com*

Abstract

We report the results of a theoretical investigation of electronic properties of ideal cation and anion vacancies in GeSe. The calculations have been performed using self-consistent Green's function method. The bulk electronic structure is described by a tight-binding Hamiltonian in the bases sets of Linear Combinations of Atomic Orbitals (LCAO). The Green's function of the perfect crystal evaluated using an eigenfunction expansion employing wave functions and band structures obtained from a self-consistent, pseudopotential, local-density-functional calculation. The defect potential is calculated using occupied electron states of the perturbed system. Results are obtained in terms of vacancy bound states, vacancy resonances, and vacancy antiresonances. The energy states in energy gaps, their origin, orbital content and resonances due to the localized defects are discussed.

Key Words: Green's function method, point defects, LCAO

1. Introduction

Various defects in crystals play an important role in their physical and chemical properties as thermodynamic, electrophysical, optical and kinetic behaviour of semiconductors. At those values of temperature and charge carrier concentration at which many semiconductor devices work, the electronic properties of semiconductors are especially sensitive to the character of various defects and their concentration. The electronic structure of shallow impurities can be described by means of the effective-mass theory. In case of strongly localized defects, radius of the wave function associated with the defect states appears reduced, or the order of the lattice constant and the effective-mass theory is not suitable. Self-consistent Green's function method has been shown [1–5] to be a powerful tool for studying deep-level impurities, electronic structure of point defects and semiconductor surfaces.

In this paper, we have calculated the electronic structure of the ideal Ge (V_{Ge}) and Se (V_{Se}) vacancies in GeSe using the self-consistent Green's function scattering-theoretical method. Due to the strong anisotropy of the chemical bonds and their physical properties, the GeSe-type $A^{IV}B^{VI}$ crystals have attracted considerable

interest [6–11], especially for their potential applications in electronic devices. In the perspectives of fabricating a non-toxic and low-cost photovoltaic system, $A^{IV}B^{VI}$ type crystals has recently received considerable interest as a potential solar cell material. Physical properties of these compounds are suitable for photovoltaic and nano-quantum well device applications. GeSe layered compounds crystallize in the D_{2h}^{16} space group of orthorhombic symmetry, with eight atoms in the unit cell. In this structure, the Ge (Se) atom is surrounded by six Se (Ge) atoms, three at a short distance with the interatomic directions almost perpendicular to each other and three at a somewhat larger distance.

2. The Green's function method

Let H^0 be the perfect crystal Hamiltonian, U be the defect potential and $H = H^0 + U$ is the one-electron Hamiltonian for the perturbed system. The one-particle Green's operator G^0 defined by

$$G^0(E) = \lim_{\varepsilon \to 0+} (E - H^0 + i\varepsilon)^{-1} \tag{1}$$

and the Green's operator G defined by

$$G(E) = \lim_{\varepsilon \to 0+} (E - H + i\varepsilon)^{-1}, \tag{2}$$

in terms of H, are related by Dyson's equation

$$G = G^0 + G^0 U G. \tag{3}$$

This equation can be solved formally to obtain

$$G = (1 - G^0 U)^{-1} G^0. \tag{4}$$

The eigenvalues of H^0 correspond to the poles in $G^0(E)$, while H has eigenvalues at energies for which H^0 has eigenvalues and at energies where $(1 - G^0 U)^{-1}$ has poles in the energy gaps.

From the above equations we obtain

$$[1 - G^0(E)U]\Psi = 0, \tag{5}$$

where Ψ is wave function of the perturbed system. Bound states correspond to the zeros of the determinant

$$D(E) = \text{Det} \left\| 1 - G^0 U \right\| = 0. \tag{6}$$

If Ψ expanded in any complete orthonormal set of states φ_α, equation (6) becomes a set of linear algebraic equations

$$\text{Det}[\delta_{\alpha\beta} - (G^0 U)_{\alpha\beta}] = 0. \tag{7}$$

For a localized potential U, only a finite number of the potential matrix elements $U_{\alpha\alpha'}$ will be different from zero.

The change in the density of states within the band continua is given by

$$\Delta N(E) = \frac{1}{\pi} \frac{d\delta(E)}{dE}, \tag{8}$$

where

$$\delta(E) = -arctg[ImD(E)/ReD(E)].$$

The change in the charge density arising from redistributions in the valence bands is given by the equation

$$\Delta\rho_V = \int_{-\infty}^{E_V} \left[\rho(E) - \rho^0(E)\right] dE = \frac{2}{\pi} Im \int_{-\infty}^{E_V} \left\{1 - \left[1 - G^0(E)U\right]^{-1}\right\} G^0(E) dE, \tag{9}$$

$$\rho^0(E) = -(2/\pi)ImG^0(E), \quad \rho(E) = -(2/\pi)ImG(E)$$

where, E_V is the top of the valence bands. This equation expresses the change in the charge density $\Delta\rho_V$ through perturbation potential U.

The total change in the charge density is given by the relation

$$\Delta\rho = \Delta\rho_V + \sum_i |\psi_i\rangle \langle\psi_i|, \tag{10}$$

where ψ_i are wave functions of the occupied discrete states in the energy gaps.

For self-consistency, the calculation is first done with a trial U. As a trial potential U, it is a pseudopotential of the vacancy atom equal in magnitude but opposite in sign [12]. The induced change in the charge density is then calculated from equation (10). This charge density is used to obtain a new U in the local-density approximation and calculation is repeated until self-consistency is achieved. The exchange-correlation effects are considered using the Perdew-Zunger scheme [13] as parameterized by Ceperley and Alder. In the charge distribution calculations the irreducible Brillouin zone (BZ) was sampled with 64 k-points using the Monkhorst-Pack [14] scheme. Since neutral defect does not create long-range Coulomb potential, the defect potential is screened completely. As seen from Figure 1, after the self-consistency the defect potential is effectively screened and localized within the space of radius 4.4 a.u., and is smaller than the distance to nearest-neighbors, 4.8 a.u.
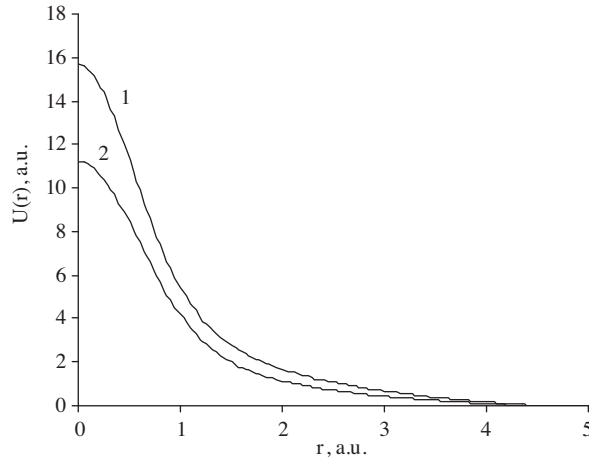

Figure 1. Screened perturbing potential of defect. Curve 1 is for V_{Se} ; curve 2 is for V_{Ge}.

3. Results and discussion

In order to calculate the Green's function of the ideal crystal, at first we carried out a band structure calculation to determine the energies and Bloch functions by pseudopotential method in plane-wave basis. In

our calculations we used the Bachelet-Hamann-Schluter [12] relativistic analytic pseudopotentials for Ge and Se, and the LDA to describe the electronic exchange-correlation interactions.

Screening and exchange-correlation effects were treated within Hubbard-Sham model with selected parameters of the charge distribution around each particular ion. A kinetic energy cut-off for the plane-wave basis-set was 16 Rydberg, which provided good convergence of the band structure calculation.

In order to represent $G^0(E)$ and U in matrix form, we used a localized basis set consisting of s, p and d functions centered on the central site and the six nearest neighbors. The radial functions were chosen to be Slater orbitals [15]. Radial functions with $\lambda_{Ge} = 1.5$, $\lambda_{Se} = 1.52$ were used for s functions, and $\lambda_{Ge} = 1.8$, $\lambda_{Se} = 1.83$ were used for p and d functions. To test convergence the calculations were repeated with additional radial functions, but the results were not essentially changed. We have computed the matrix elements of $G^0(E)$ and U in reciprocal space. For this purpose, we expand the localized orbitals in plane waves. Fourier transform of the Slater orbitals easily derived in an analytical form. Once the expansion coefficients are known, all matrix elements can be calculated in plane-wave representation.

Point group C_{1h} of the cation and anion vacancies consists of: {E}, identical element; {σ_v}, reflection plane perpendicular to the x-axis, passing through vacancy (the axes are chosen as in [16]). Group-theoretical analysis shows that all defect states do not degenerate and are either symmetric or antisymmetric with respect to the mirror plane.

In Figure 2 we show the calculated charge density of the ideal crystal, the charge density in a crystal containing an anion vacancy, and the change in the charge density produced by the introduction of the vacancy. As seen from figure, the change in the charge density is localized almost within the space between nearest neighbors.
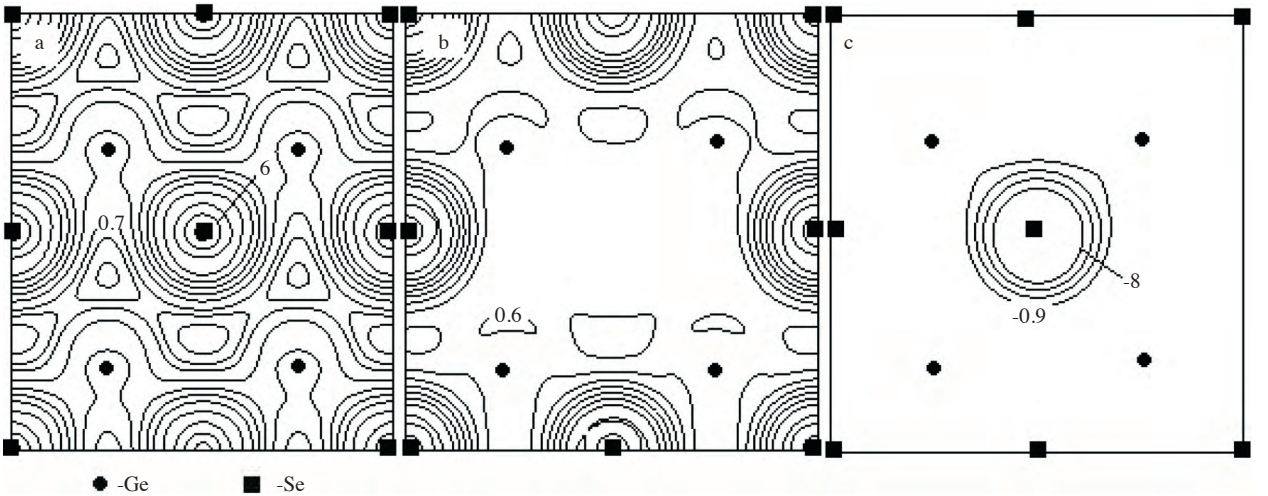

● -Ge   ■ -Se

Figure 2. Charge density in the (010) plane (in electrons per bulk unit cell) for GeSe: (a) shows charge density of an ideal crystal; (b) shows charge density in the presence of the Se-vacancy; and (c) shows the change in the charge density.

The vacancy introduces a repulsive potential corresponding to the removal of an anion or cation potential; as a result states shift to higher energies. The upper valence bands give rise to bound states in the fundamental band gap at $E_V + 0.15$ eV for V_{Ge} and at $E_V + 0.23$ eV for V_{Se}. The lower valence bands about -12 eV give rise to localized state at $E_V - 12.1$ eV for V_{Ge}. Localized states in the fundamental band gap for both V_{Ge} and

V_{Se} are empty. Analyzing the character of defect-related wave functions, we find the states in the fundamental band gap to be antisymmetric while the state at $E_V - 12.1$ eV is symmetric.

Analysis of the wave functions and charge density associated with the localized states of cation and anion vacancies (Figure 3) reveals that the states in the fundamental gap primarily consist of p-like orbitals centered on the nearest neighbors, whereas the state at about $E_V - 12.1$ eV primarily consist of s-like orbitals centered on the nearest neighbors and can be characterized as back bonds of the three nearest-neighbour atoms. It is consistent with the fact that the upper valence bands originate mainly from the anion and cation p-states, whereas the lower valence bands originate primarily from anion s-states [7].
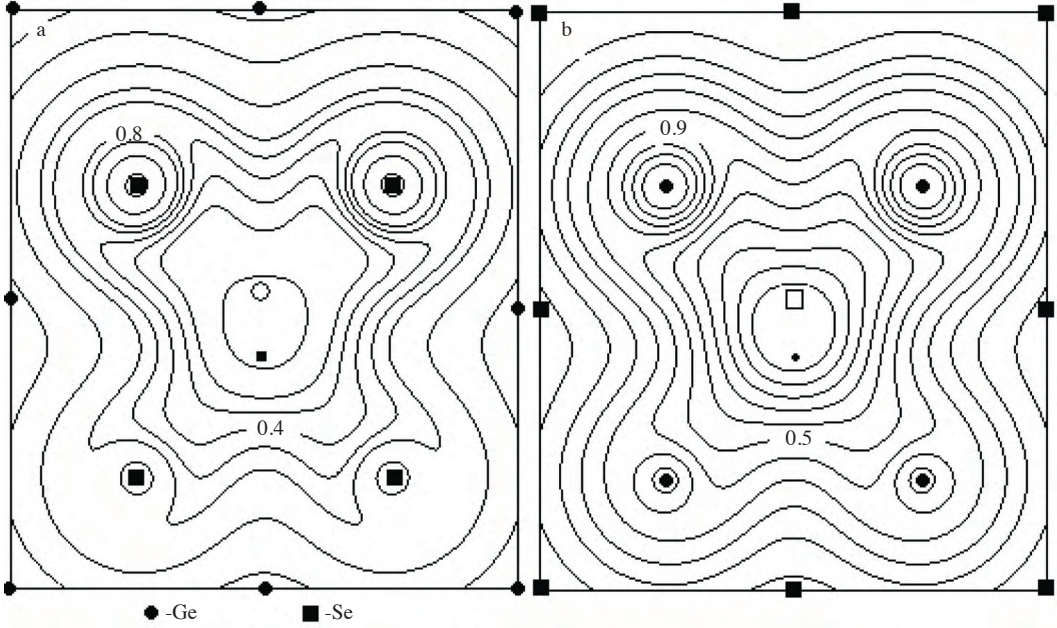

Figure 3. Charge density in the (010) plane (in electrons per bulk unit cell) associated with the (a) Ge-vacancies (located by the open circle ◯ at the center of the left plot) and (b) with Se-vacancies (located by the open square at the center of the right plot).

Distribution of charge density of the localized states in the fundamental band gap of V_{Ge} and of V_{Se} have a similar picture, though localization of V_{Se} states due to stronger defect potential (Figure 1) higher, than corresponding V_{Ge} states. This is because of cations and anions have identical atomic geometry in an ideal crystal: cation atoms form distorted octahedron around of anion atoms, and vice versa. The anion (cation) vacancy is surrounded by three low-coordinated cation (anion) atoms; two in the first layer and one in the second layer. The atomic structure of both cation and anion vacancies maintains the C_{1h} symmetry. Wave functions of all deep levels exponentially decay at removal from vacancy. Symmetry and origin of these defect states can be qualitatively explained in terms of LCAO models. In LCAO models of an ideal crystal [16], using atomic orbitals centered on every atoms it is constructed hybrid orbitals, directed along bonds of the nearest neighbors of the given atom. From this orbitals, then form bonding and antibonding orbitals, which give rise to the valence and conduction bands, respectively. For the crystal containing vacancy, the nearest neighbors of vacancy cannot create bonding and antibonding orbitals and these orbitals remain "dangling." As a first approximation one would expect that, localized states are linear combinations of these "dangling hybrids."

Actually, our calculations show that the localized states are primarily a linear combination of these dangling hybrids.

Except the localized states in the fundamental gap, within the band continua there are defect-induced resonances and antiresonances. The antiresonance at $E_V - 5.2$ eV for V_{Se} appears in a point where density of states of an ideal crystal has a minimum and consequently it corresponds to critical points of band structure and therefore is quasi-resonance. Features at $E_V - 3.7$ eV for V_{Se} and at $E_V - 3.2$ eV for V_{Ge} are determined by own nature of defect potential and therefore are resonances. From analyzing the wave functions we find that resonances also mainly consisting of p-states centred at the three neighbours.

In accordance with our calculations in [8] it is shown, that presence of cation vacancies in GeSe cause p-type conductivity and formation of impurity states in fundamental band gap.

Acknowledgements

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