

ELECTRONIC STRUCTURE OF THE Ge VACANCIES IN GeSe LAYERED SEMICONDUCTOR

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The electronic structure of the cation vacancies in GeSe is evaluated using the self-consistent Green's function method in bases sets of Linear Combinations of Atomic Orbitals (LCAO). The energy states in energy gaps, their origin, orbital content and resonances due to the localized defects are discussed.

Keywords: electronic structure, Green's function method, vacancies, LCAO.

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Various defects in crystals play an important role in their physical and chemical properties as thermodynamic, electrophysical, optical and kinetic behaviour of semiconductors. At values of temperature and concentration of charge carrier at which many semiconductor devices work, electronic properties of semiconductors especially sensitive to character of various defects and their concentration. The electronic structure of shallow impurities can be described by means of the effective-mass theory [1]. In case of strongly localized defects, the radius of wave function of the defect states appears less or the order of the lattice constant and the effective-mass theory not suitable. Self-consistent Green's function method has been shown [2-5] 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}) 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 nanoquantum-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 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 [12].

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

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

and the Green's operator G is defined by

$$G(E) = \lim_{\varepsilon \rightarrow 0^+} (E - H + i\varepsilon)^{-1} \quad (2)$$

in terms of H are related by Dyson's equation

$$G = G^0 + G^0 U G \quad (3)$$

This equation can be solved formally to obtain

$$G = (I - G^0 U)^{-1} G^0 \quad (4)$$

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

From the above equations we obtain,

$$[I - G^0(E) U] \Psi = 0 \quad (5)$$

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

$$D(E) = \text{Det} \| I - G^0 U \| = 0 \quad (6)$$

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

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

Since a potential U is strongly localized in a nearby of defect, if localized functions to use as a basis set, the order of a determinant of (6) will be determined by the number of nearest-neighbors for which $U_{\alpha\alpha}$ is nonzero.

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

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

where

$$\delta(E) = -\text{arctg} [Im D(E) / Re D(E)]$$

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

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

$$\rho^0(E) = -(2/\pi)\text{Im}G^0(E) , \rho(E) = -(2/\pi) \text{Im}G(E)$$

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

$$\Delta\rho = \Delta\rho_V + \sum_i |\psi_i\rangle\langle\psi_i| \quad (10)$$

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 chosen pseudo potential of the vacancy atom equal in magnitude but opposite in sign [13]. The induced change in the charge density is then calculated from equations (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 [14] as parametrized by Ceperley and Alder. In the charge distribution calculations the irreducible Brillouin zone (BZ) was sampled with 64 k - points using the Monkhorst-Pack [15] scheme. Since neutral defect does not create long-range Coulomb potential, the defect potential is screened completely. As seen from fig. 1, after the self-consistency the defect potential is effectively screened and localized within the space in radius 4.4 a.u., i.e. smaller, than distance up to nearest-neighbors, equal 4.8 a.u.

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 pseudo potential method in plane-wave basis. In our calculations were used non-local ionic pseudopotentials built up in the scheme suggested by Bachelet et al. [13]. Good convergence has been obtained for the band structure calculation with the choice of a kinetic energy cut-off at 16 Rydberg.

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 [16]. Radial functions with $\lambda_{Ge}=1.5$, $\lambda_{Se}=1.52$ were used for s functions and with $\lambda_{Ge}=1.8$, $\lambda_{Se}=1.83$ 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 vacancies consists of: $\{E\}$, identical element; $\{\sigma_v\}$, reflection plane perpendicular to the x axis, passing through vacancy (the axis are chosen as in [17]). Group-theoretical analysis shows that all defect states not degenerate and are either symmetric, or anti-symmetric with respect to the mirror plane.

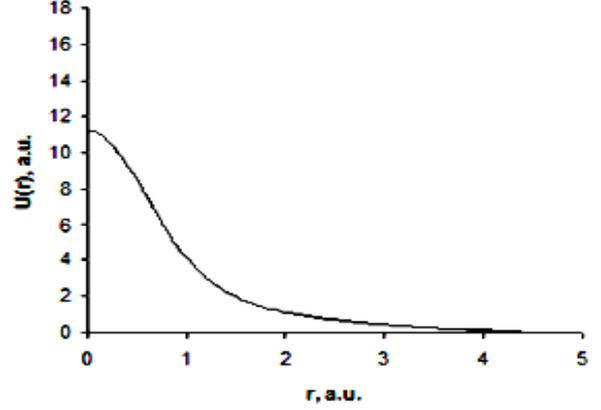


Fig. 1. Screened perturbing potential of V_{Ge} defect.

In fig. 2 we show the calculated charge density of the ideal crystal. 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 $E_V + 0.31$ for V_{Ge} . The lower valence bands about -12 eV give rise to localized state at $E_V + 0.31$ for V_{Ge} . Localized states in the fundamental band gap for both V_{Ge} are empty. Analyzing the character of defect-related wave functions, we find the states in the fundamental band gap to be anti-symmetric while the state at $E_V + 0.31$ is symmetric.

Analysis of the wave functions and charge density associated with the localized states of cation vacancies (fig. 3) reveals that the states in the fundamental gap consist primarily of p - like orbitals centered on the nearest neighbors, whereas the state at about $E_V + 0.31$ consist primarily 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, 17].

The cation vacancy is surrounded by three low-coordinated anion atoms; two in the first layer and one in the second layer. The atomic structure of cation vacancy 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.

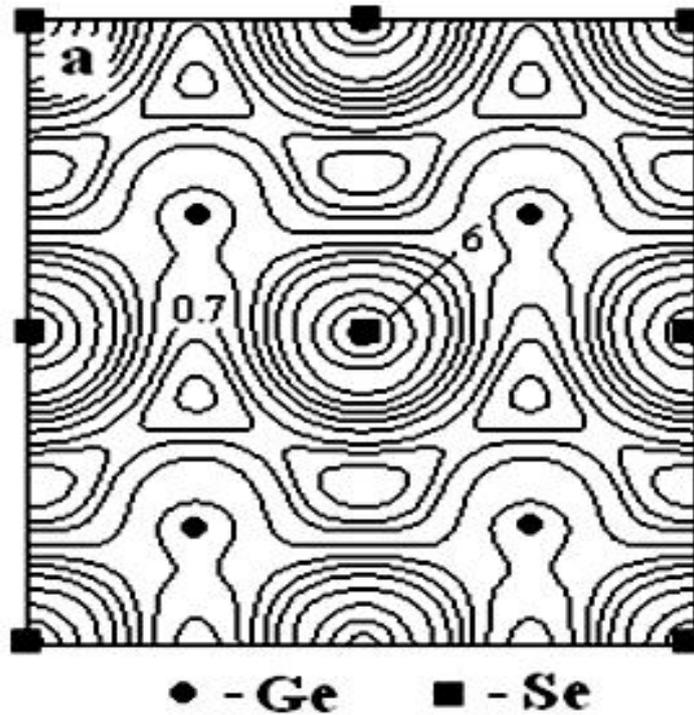


Fig. 2. Charge density in the (010) plane (in electrons per bulk unit cell) for GeSe.

In LCAO models of an ideal crystal [17], 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 anti-bonding 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 anti-bonding 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 anti-resonances. Features at $E_V + 0.31$ 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 consisting mainly of p - states centred at the three neighbours.

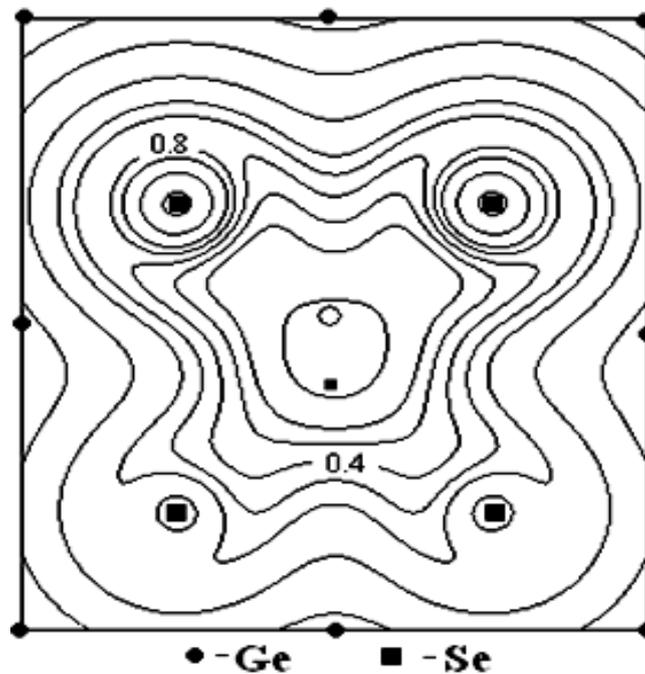


Fig. 3. Charge density in the (010) plane (in electrons per bulk unit cell) associated with the Ge -vacancy.

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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.

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