

Ab initio modeling of optical properties of the new sp^3 silicon and germanium allotropes

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Abstract

The application of the hybrid topological-quantum-mechanical method to the search of new allotropes of 14th group elements is demonstrated for silicon and germanium. Starting from the databases of hypothetical and real zeolite nets and subsequently applying the geometrical and energetic selection criteria, we extract the most energetically favourable structures for the allotropic modifications of silicon and germanium, and study their optical properties. In the framework of density functional theory we calculate the frequency-dependent complex dielectric tensors, refraction and absorption coefficients of the selected allotropes and their electronic band gaps.

Keywords: crystal structure design; photonics; density functional theory; silicon and germanium optic properties.

1. Introduction

The elements of XIVth group of the periodic table (carbon, silicon and germanium) are widely used in the modern electronics, photonics and photovoltaics, as functional elements of the different electronic and optical devices. Of particular importance are their optical properties in the sense of absorption and refraction of the incident electromagnetic radiation of different wavelength ranges: infrared (IR), visible and ultraviolet (UV). The properties of carbon, silicon and germanium crystals with the diamond crystal lattice (the space group $Fd\bar{3}m$) have been studied quite well, both experimentally [1] and theoretically [2]. One of the tasks of theoretical material science based on quantum ab initio calculations is the search and prediction of new allotropic modifications of carbon, silicon and germanium, which would have a set of properties exceeding diamond structures. These new structures are of interest in the practical applications to solve various problems of micro- and nanoelectronics, photonics and photovoltaics.

2. Computer design of new allotropes

There are four main steps in this theoretical study: the search for new crystalline structures, the verification of their stability under normal or specified conditions, the calculation of the basic physical properties, and the search for the ways of their synthesis. In our work we use a new method of search for new allotropic modifications, based on topological analysis of the modern bases of hypothetical zeolite nets [3,4]. For the first time this method was used in our work [5] to search for the carbon allotropes with sp^3 -hybridization of chemical bonds, close in energy and other physical properties to diamond. We analyzed more than 600 thousand zeolite nets, applying subsequently topological and geometric selection criteria. As an example of such a criterion, at one stage we excluded from consideration all structures containing 3 and 4-membered rings, since the presence of such chains of bonds in carbon allotropes leads to a significant internal stress in the structure. Then we relaxed the positions of atoms in the structures using quantum-mechanical modeling packages and selected those structures in which the sp^3 -hybridization of chemical bonds was preserved. For them, we calculated the binding energies of the ground state and compared them with the energy of the diamond configuration, selecting 6 most advantageous structures, with binding energy per atom not more than 0.12 eV compared to diamond. Taking into account the chemical relation of carbon, silicon and germanium, it is obvious to assume that the same allotropic modifications (from the point of view of crystallography, that is, with the same symmetry group and topology) exist for silicon and germanium. In Table 1 we give the chemical bond lengths, the angles between them, the distances to the nearest neighbors for the predicted allotropes of silicon and germanium.

Table 1. Chemical bond lengths, bond angles, the distances to the nearest neighbors for the predicted allotropes of silicon and germanium. Definitions are the same as in the work [5].

Silicon

| Structure | Bond lengths, Å | Bond angles, degrees | Nearest-neighbor distances, Å |
|-----------|-----------------|----------------------|-------------------------------|
| #26 | 2.308-2.382 | 95.98-126.34 | 3.818 |
| #27 | 2.308-2.415 | 95.31-125.84 | 3.820 |
| #28 | 2.308-2.406 | 93.14-124.12 | 3.818 |
| #50 | 2.301-2.386 | 96.95-127.46 | 3.826 |
| #55 | 2.322-2.422 | 97.91-120.04 | 3.828 |
| #88 | 2.322-2.380 | 98.16-119.32 | 3.837 |

Germanium

| Structure | Bond lengths, Å | Bond angles, degrees | Nearest-neighbor distances, Å |
|-----------|-----------------|----------------------|-------------------------------|
| #26 | 2.436-2.562 | 94.76-126.16 | 4.055 |
| #27 | 2.436-2.533 | 94.76-126.16 | 4.055 |
| #28 | 2.447-2.539 | 92.88-120.79 | 4.057 |
| #50 | 2.439-2.530 | 96.29-122.11 | 4.067 |
| #55 | 2.451-2.547 | 98.65-119.12 | 4.058 |
| #88 | 2.459-2.514 | 97.51-120.61 | 4.068 |

3. Calculation methods

The recent development of methods for quantum mechanical calculations of energy and the electron density distribution of many-electron systems (atoms, molecules, crystals) is associated with the success of density functional theory (DFT) [6,7,8] and combined or hybrid methods based both on DFT and the Hartree-Fock (HF) approach [9], which take into account the exchange interaction more accurately than the DFT. Quantum mechanical calculations of the physical properties of crystals require a significant computational resources, in comparison with atomic or molecular calculations, and can be performed only on supercomputers or multiprocessor cluster systems. In our work, we use the most common and widely used licensed software packages CRYSTAL [10] and VASP [11], installed on the supercomputer "Sergey Korolev" of the Samara University. The CRYSTAL software package uses a basis of atomic orbitals and an all-electron approximation, while the VASP package uses a basic set of plane waves and a pseudopotential approximation.

To check the stability of the predicted silicon and germanium allotropes, the matrices of elastic constants and various elastic coefficients were calculated, and we showed the structures to be mechanically (energetically) stable at zero external pressure (see Fig. Tables 2 and 3). We also demonstrated the absence of imaginary frequencies in the phonon spectra of studied silicon and germanium allotropes. As an example, Fig. 1 shows the calculated phonon spectrum for the allotrope Si#50. All calculations were performed in the generalized gradient approximation (GGA) of the density functional theory with the exchange-correlation functional PBE [12].

Table 2. Density, binding energy difference, band gap, band gap in Gamma point, bulk modulus, bulk modulus derivative, shear modulus and static dielectric constants for silicon allotropes.

| GGA PBE | 88,Pnma | 50,Pnma | 55,Pmma | 26,P2/m | 27,C2/m | 28,Pbam |
|--------------------------------------|---------|---------|---------|---------|---------|---------|
| ρ g/cm ³ | 2.293 | 2.291 | 2.305 | 2.298 | 2.291 | 2.271 |
| ΔE , eV | 0.037 | 0.036 | 0.035 | 0.039 | 0.047 | 0.036 |
| E_{gap} , eV | 1.40 | 1.42 | 1.26 | 0.97 | 1.02 | 1.31 |
| $\Delta E_{gap}(\Gamma-\Gamma)$, eV | 1.56 | 1.51 | 1.58 | 1.10 | 1.12 | 1.57 |
| B, GPa | 78 | 84 | 83 | 84 | 84 | 86 |
| B' | 2.74 | 4.31 | 3.75 | 4.14 | 4.35 | 4.64 |
| G, GPa | 48 | 48 | 48 | 50 | 51 | 51 |
| ϵ_{xx} , | 11.88, | 11.92, | 11.74, | 11.85, | 12.74, | 12.55, |
| ϵ_{yy} , | 12.05, | 12.05, | 11.40, | 11.78, | 11.94, | 11.51, |
| ϵ_{zz} | 12.09 | 12.52 | 11.87 | 12.18 | 12.07 | 11.93 |

Table 3. Density, binding energy difference, band gap, band gap in the Gamma point, bulk modulus, bulk modulus derivative, shear modulus and static dielectric constants for germanium allotropes.

| GGA PBE | 88,Pnma | 50,Pnma | 55,Pmma | 26,P2/m | 27,C2/m | 28,Pbam |
|--------------------------------------|---------|---------|---------|---------|---------|---------|
| ρ , g/cm ³ | 5.251 | 5.086 | 5.121 | 5.102 | 5.087 | 5.054 |
| ΔE , eV | 0.037 | 0.038 | 0.036 | 0.044 | 0.052 | 0.033 |
| E_{gap} , eV | 0.87 | 0.86 | 0.61 | 0.42 | 0.23 | 0.65 |
| $\Delta E_{gap}(\Gamma-\Gamma)$, eV | 0.95 | 0.96 | 1.08 | 0.42 | 0.60 | 0.65 |
| B, GPa | 57 | 59 | 59 | 59 | 59 | 60 |
| B' | 4.24 | 4.54 | 4.38 | 4.44 | 4.53 | 4.61 |
| G, GPa | 43 | 43 | 44 | 45 | 45 | 46 |
| ϵ_{xx} , | 14.87, | 15.69, | 14.77, | 15.57, | 16.74, | 16.07, |
| ϵ_{yy} , | 16.47, | 16.38, | 15.31, | 15.92, | 17.77, | 14.82, |
| ϵ_{zz} | 15.74 | 16.18 | 15.49 | 15.51 | 16.76 | 15.50 |

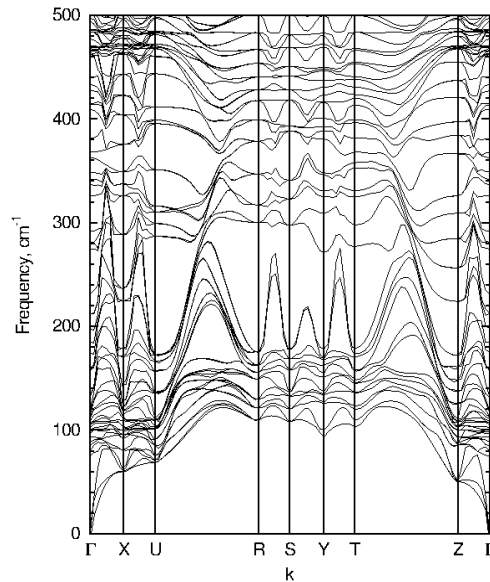


Fig.1. The calculated phonon spectrum of allotrope Si#50 along the high-symmetry pathway in the reciprocal space.

4. The optical properties of allotropes

Methods for calculating the optical properties of crystals depend on the chosen electromagnetic wavelength range. The properties of the complex dielectric tensor in the infrared region are determined in the semi-classical Drude-Lorentz theory by singularities of the crystal lattice vibration spectrum, which can be calculated in the quasi-harmonic approximation [13] with the transverse and longitudinal optical vibration modes. The spectrum of eigenfrequencies of allotropes allows one to calculate their Raman scattering spectra and absorption spectra in the IR range. Investigation of Raman spectra can be used for experimental search for new allotropic modifications, since the position of the Raman peaks is uniquely related to the structure of the crystal lattice, the forces and lengths of the chemical bonds. Unlike the diamond modification of silicon, the Raman spectra of its allotropic modifications have a more complex structure, which makes it difficult to identify them experimentally. At the same time, the Raman spectra of germanium allotropes, like the Raman spectrum of the diamond modification of germanium, have only one strong peak, which is significantly shifted relative to the peak at a frequency of about 300 sec^{-1} , which is observed for the ground state of germanium, Fig. 2. It is well known that diamond and diamond-like crystals of silicon and germanium practically do not absorb in the IR range. The silicon and germanium allotropes predicted by us have narrow absorption bands in the IR range, which can also be used for their experimental search and identification, see Fig. 3.

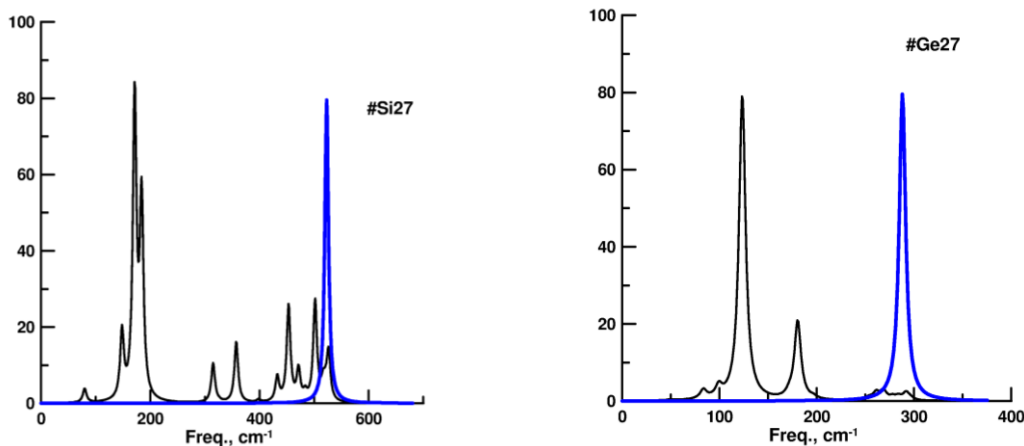


Fig. 2. Raman shift spectra for allotropes of silicon (Si#27) and germanium (Ge#27) – black curves, diamond-like silicon and germanium – gray curves.

The electronic band structure of a crystal determines the properties of its complex dielectric function, hence, the dependence of the absorption and refraction coefficients on the frequency of electromagnetic radiation in the visible and UV ranges. DFT allows to obtain a microscopic dielectric function in the random phase approximation within the theory of linear response, in the visible and ultraviolet frequency ranges. Neglecting the local field effects, we can derive from the microscopic dielectric function a macroscopic dielectric function. The imaginary part of the latter is a tensor and can be written in the form of a weighted sum over transitions between levels, and the real part is obtained from the imaginary one using the Kramers-Kronig relations. We can extract both the optical constants and the complex dielectric function averaged over the directions directly from the components of the macroscopic dielectric tensor, which allow us to determine the optical absorption and refraction spectra for the studied structures.

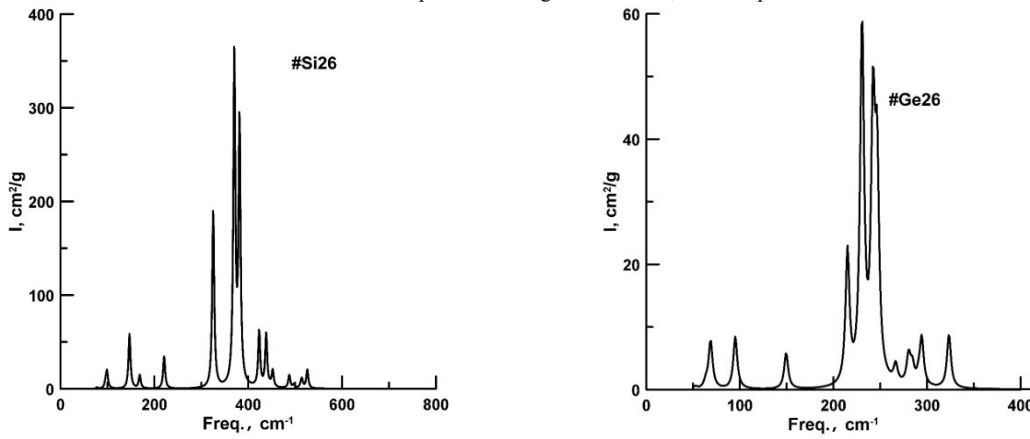


Fig. 3. Infrared absorption spectra for allotropes of silicon (Si#26) and germanium (Ge#26).

The electronic band gap of a semiconductor determines the energy boundary of absorption of optical photons. It is known that standard DFT methods do not allow to reproduce this gap correctly, in particular for materials with a narrow optical gap, such as germanium. Therefore, in our calculations we used the hybrid functional HSE06 [14], which allows to obtain results comparable to the experimental data. However, the standard functional PBE is more adequate in describing the position of the peaks of the complex dielectric function. Tables 2 and 3 show the calculated values of the band gaps (indirect and in the Gamma point of the reciprocal space) and the permittivity coefficients of silicon and germanium allotropes, respectively. We note that the small value of the band gap of the allotrope Ge#27, 0.23 eV, may indicate metallization of this structure at high temperatures and loss of semiconductor properties. In Fig. 4 we present an electronic band structure for the allotrope Si#27 and Ge#27.

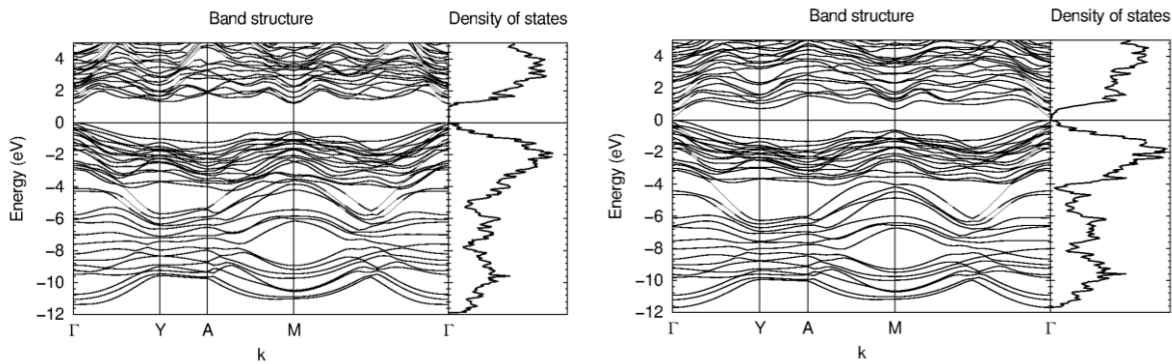


Fig.4. The electronic band structure of the allotropes Si#27 (left) and Ge#27 (right), calculated along the high-symmetry pathway in the reciprocal space, and the corresponding electron density of states.

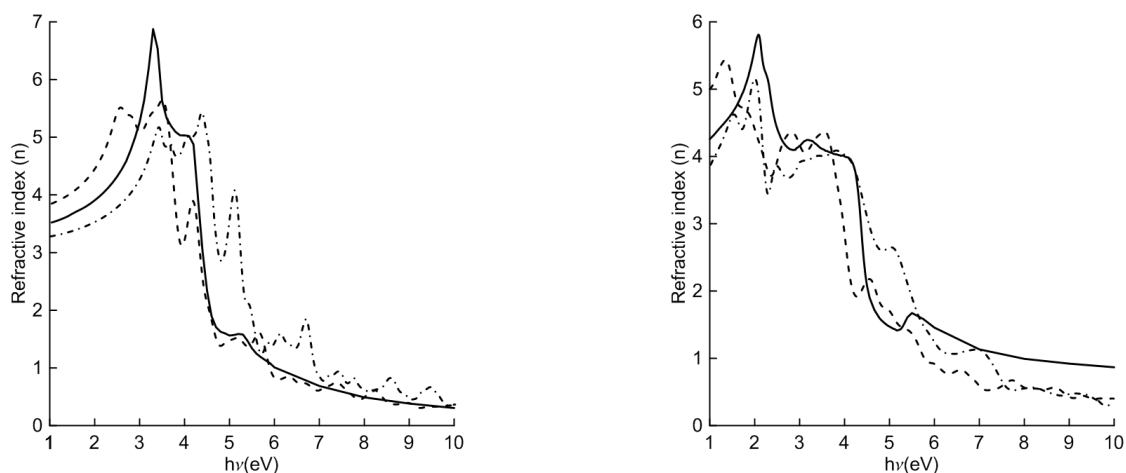


Fig. 5. The refractive index for diamond configurations of silicon (left) and germanium (right). Dash-dotted line – the results obtained for the functional HSE06, the dashed line – for the functional PBE, solid line – experimental data [1].

In Fig. 5 we show the calculated (dash-dotted line – HSE06, dashed – PBE) curves in comparison with the experimental data (black line) of the frequency-dependent refractive indices n for diamond configurations Si (left) and Ge (right). The absorption spectra (k), together with the relative spectrum of solar irradiation at the reference air mass of 1.5, are shown in Fig. 6, respectively. Amorphous forms of Si and Ge, the so-called a-Si and a-Ge, as well as their various hydrogenated forms and some Si-Ge compounds [1] demonstrate promising properties for use in electronics and photovoltaics, especially in solar cells.

Comparing the results for our allotropes for the refraction and absorption coefficients with the corresponding spectra of amorphous forms, we observe quantitative and qualitative agreement both for the position of the refraction/absorption peak and for its absolute value (see Figures 7 and 8). This can be an evidence that the predicted by us allotropes can be a counterpart of the corresponding amorphous forms.

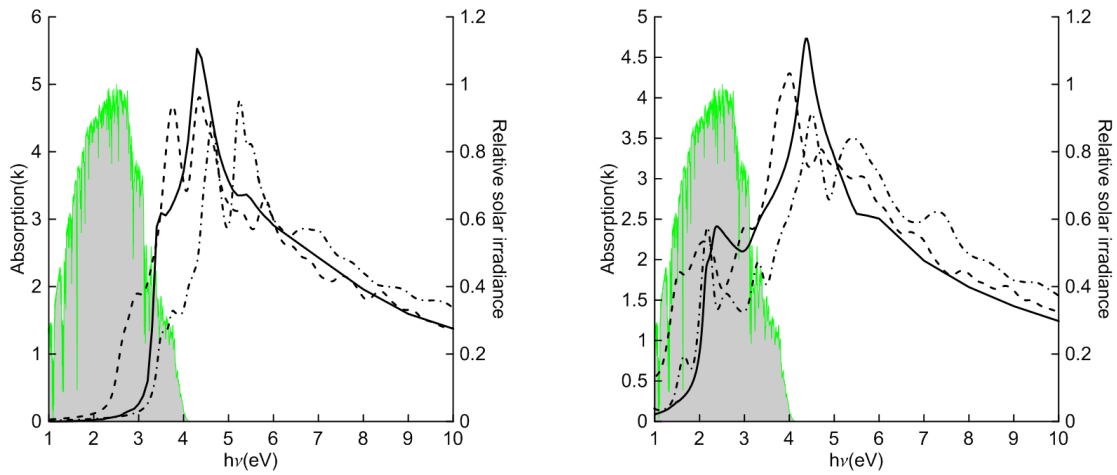


Fig. 6. The absorption index for diamond configurations of silicon (left) and germanium (right). Dash-dotted line – the results obtained for the functional HSE06, the dashed line – for the functional PBE, solid line – experimental data [1]. The shaded area is the relative spectrum of solar irradiance at the reference air mass of 1.5.

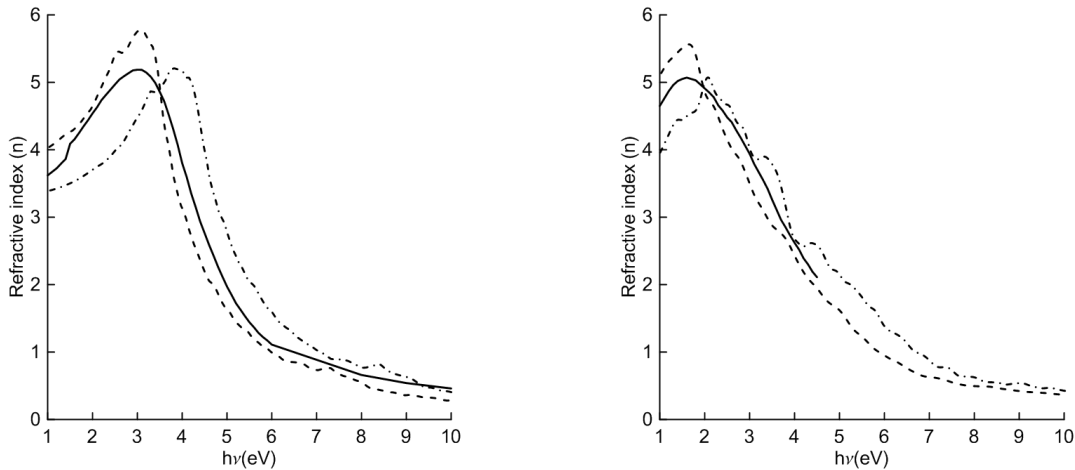


Fig. 7. The refractive index for allotropes #28 of silicon (left) and germanium (right). Dash-dotted line – the results obtained for the functional HSE06, the dashed line – for the functional PBE, solid line – experimental data for the amorphous forms [1].

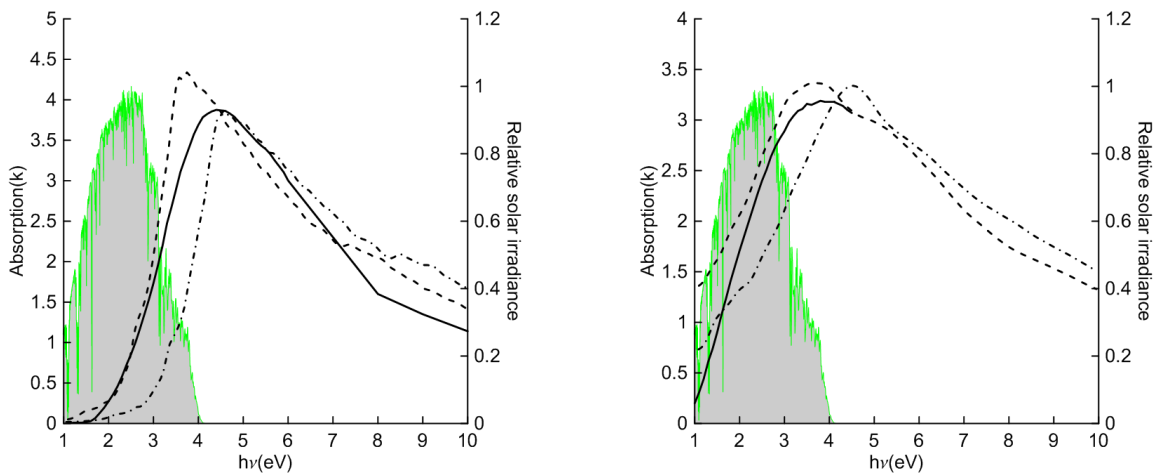


Fig. 8. The absorption index for allotropes of silicon (left) and germanium (right). Dash-dotted line – the results obtained for the functional HSE06, the dashed line – for the functional PBE, solid line – experimental data [1] for the amorphous forms. The shaded area is the relative spectrum of solar irradiance at the reference air mass of 1.5.

5. Conclusions

We investigated the six new low-energy allotropes of silicon and germanium [15], isostructural to the previously proposed carbon allotropes [5], demonstrating an application of the hybrid topology-quantum-mechanical approach [5] to prediction of new structures. Using the *ab initio* methods implemented in the CRYSTAL [10] and VASP [11] software packages, we calculated their mechanical, electronic and optical properties, which mostly resemble the properties of diamond configurations, but the observed differences in Raman shift spectra and infrared absorption spectra can allow to identify these allotropes if they are present in mixed phases. We have shown that the optical properties of allotropes under study are quantitatively and qualitatively close to the properties of amorphous modifications, a-Si and a-Ge. This leads to the conclusion that the considered allotropes are present in the experimentally observed amorphous phases, which are promising materials for electronics and photovoltaics.

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