

Supplemental material to the article

Germanium–vacancy color center in isotopically enriched diamonds synthesized at high pressures

1. Synthesis.

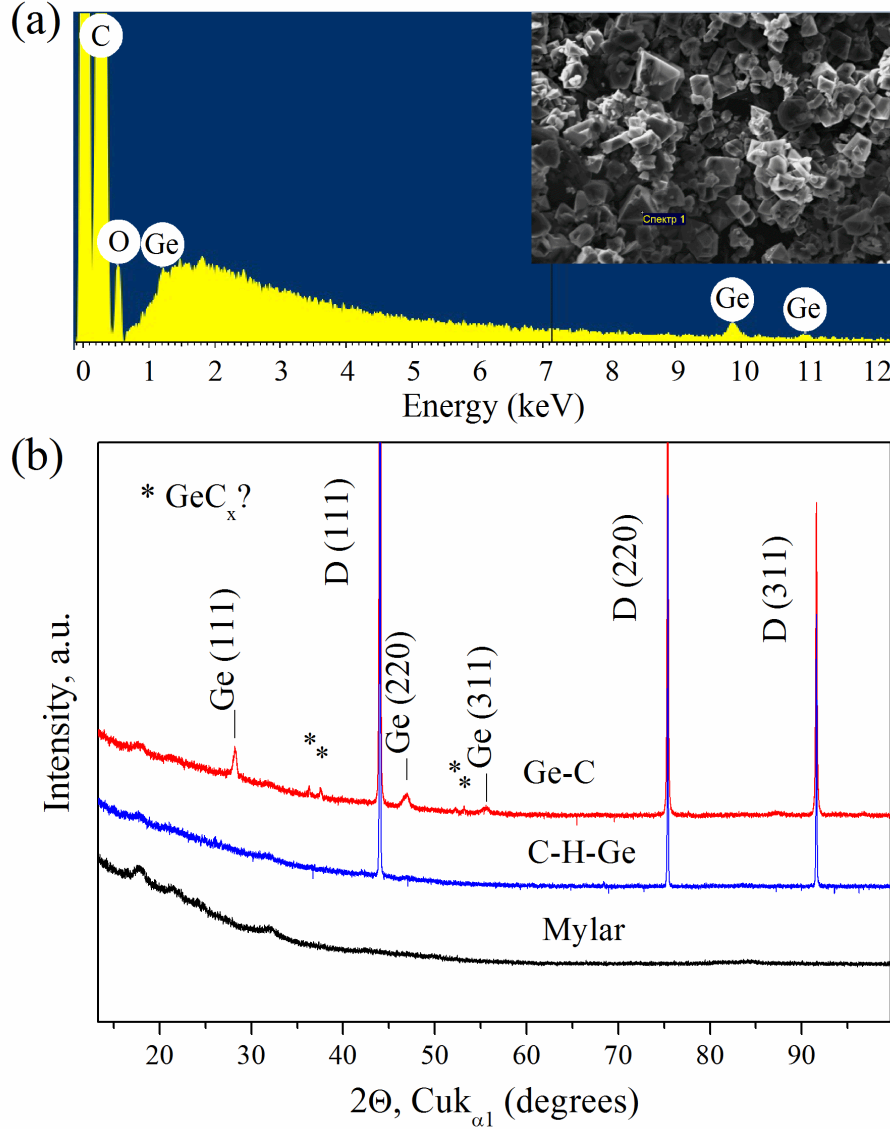


Figure 1: Ge-doped diamonds synthesized at high pressures. (a) – Chemical composition of a diamond crystal, as-synthesized in the C–H–Ge growth medium. No metal-base impurities were detected by EDX microanalysis; silicon concentration in the reaction volume was below detecting limit, 0.1–0.2 %. (b) – X-ray diffraction analysis of acid-treated diamonds synthesized in the Ge–C and C–H–Ge growth systems. No secondary phases were found in diamond synthesized in the C–H–Ge system, while Ge-based inclusions were revealed in diamond produced in the Ge–C system. The diffraction lines of Ge ($Fd3m$, PDF # 040545) are shifted to higher diffraction angles indicating the compressed state of germanium inclusions. Note that molar volume of germanium expands upon crystallization

2. Optical measurements.

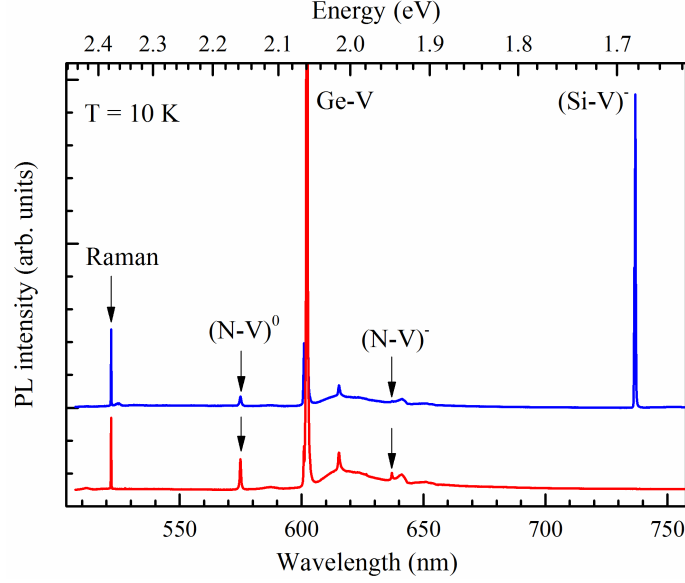


Figure 2: Photoluminescence (PL) spectra at 10 K with all main features: Ge-related zero-phonon line (ZPL) at 602 nm, the Raman peak from diamond, the $(N-V)^0$ and $(N-V)^-$ peaks at 575 and 637 nm, respectively, and the $Si-V^-$ peak at 737 nm. The presence of silicon impurity in our Ge-doped diamonds was easily eliminated by using a plexiglass mortar (the lower red spectrum) instead of a jasper one (the upper blue spectrum). The spectra are normalized to the intensity of the diamond Raman peak and displaced vertically for clarity

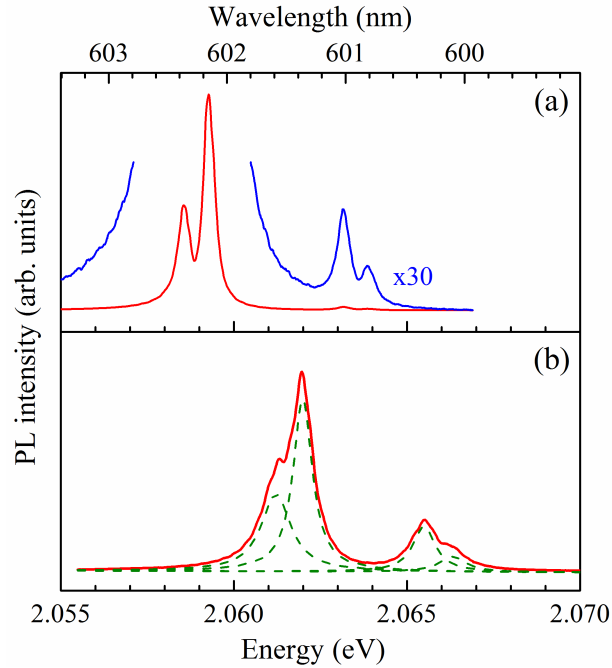


Figure 3: Carbon isotope shift in the fine structure of the ZPL. On changing the ^{13}C content from 1.1 % in natural carbon (a) to 99 % (b), we observed isotope shift +2.8 meV for ZPL of the Ge-related color center. For the synthesis of diamond enriched with the isotope ^{13}C , about 12 mass % of H_2O were added to the mixture of amorphous carbon powder and natural germanium

3. About the effective masses. For the samples with several isotopes of Ge, a peak associated with the localized vibrational mode (LVM) is the sum of the contours from each isotope, with the appropriate weight. The observed isotopic shifts of ZPL and LVM for these samples are compared with the calculated ones in the framework of a local oscillator model, taking into account the effective masses m^* of the used germanium isotopes, introduced as follows:

$$\sqrt{\frac{1}{m^*}} = \sum_i n_i \sqrt{\frac{1}{m_i}}.$$

Here, i runs over all isotopes of Ge, n_i is the concentration of the i^{th} isotope, and m_i is the mass of this isotope [S1]. In the experiment, we used pure ^{72}Ge (99.98 %), Ge with natural abundance of the isotopes (36.5 % ^{74}Ge , 27.4 % ^{72}Ge , 20.5 % ^{70}Ge , 7.8 % ^{73}Ge , 7.8 % ^{76}Ge), and almost pure ^{76}Ge (88 % ^{76}Ge , 12 % ^{74}Ge). Thus, the effective masses are $m_{72} = 71.9221$; $m_{n\text{-Ge}}^* = 72.6035$; and $m_{76}^* = 75.6407$, respectively.

4. Concentration of the $(\text{Si-V})^0$ and $(\text{Si-V})^-$ centers, and estimates for Ge-V.

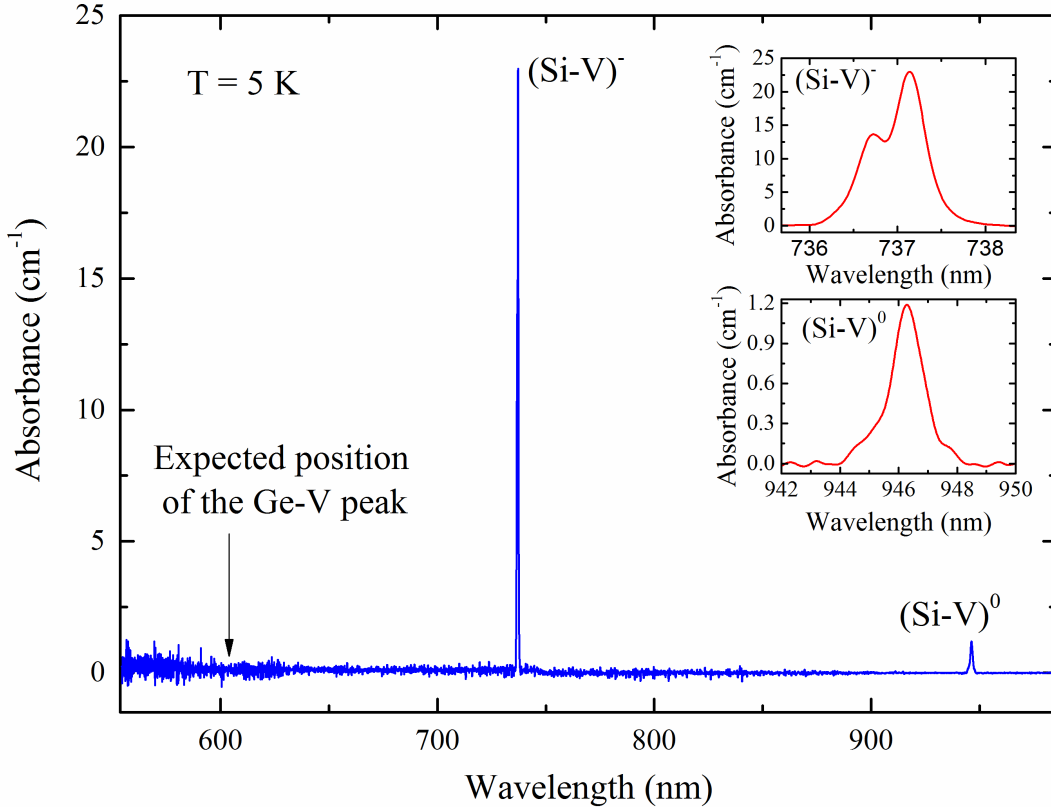


Figure 4: Absorption spectra of a diamond sample with the Si impurity. The peak absorption is 23 cm^{-1} for the $(\text{Si-V})^-$ center and 1.2 cm^{-1} for the $(\text{Si-V})^0$ one. We didn't observe any absorption line near 602 nm, where the Ge-V peak could be expected

In addition to the PL experiments, we have undertaken an attempt to register the absorption spectra of the Ge-V centers (see Fig. 4). In order to increase the optical path, a KBr tablet was prepared with effective thickness of the sample $200\text{ }\mu\text{m}$. As a result, when jasper mortar was used for the sample preparation, we were able to detect the absorption lines belonging to $(\text{Si-V})^-$ and $(\text{Si-V})^0$ with concentrations $7 \cdot 10^{15}$ and $8 \cdot 10^{15}\text{ cm}^{-3}$, respectively (according to [S2]). We observe the fine structure of the $(\text{Si-V})^-$ center at low temperatures, which also demonstrates a high quality of

the obtained crystals. However, Ge–V lines were not observed in any of the measured samples. We assume that the absence of the absorption lines of the Ge–V centers can be associated with a very low concentration of these centers. In this case, a strong luminescence of the Ge–V center may indicate a high quantum yield of the luminescence. By a comparison with the luminescence and absorption of the $(\text{Si-V})^-$ centers present in the same samples, we can give an upper estimate $< 5 \cdot 10^{14} \text{ cm}^{-3}$ for the concentration of the Ge–V centers.

5. Calculations. Basically, split-vacancy color center can be considered as two adjacent vacant sites (divacancy) with impurity atom introduced as substitutional defect which occupies one of these vacant sites. It follows from symmetry considerations that any divacancy in the diamond lattice should involve a lowering of the crystal symmetry from $Fd\bar{3}m$ to, at least, $R\bar{3}$. If one of the divacancy sites is occupied by a dopant (this geometry was taken as an initial step in the DFT calculation) the symmetry should be lowered even more (at least to $P3$). Taking into account these considerations, it seems natural to choose a supercell compatible with this broken symmetry. This supercell has some similarity to the crystal structure discussed before in [S3]. We should note the difference of our supercell geometry and ones used in previous works where the supercell was formed as two or three times multiple of original cubic cell in three directions. In the latter case, the periodicity of supercell induces additional mirror symmetry of defects ordering.

The point group symmetry is $C_{3i}(\bar{3})$. Its irreducible representations are one-dimensional and degeneracy of defect levels is caused by the fact that $^1E_g/{}^2E_g$ on the one hand and $^1E_u/{}^2E_u$ on the other (corresponding to upper and lower pairs of defect levels, respectively) are complex conjugate, so they should have the same Kohn–Sham eigenvalues. As it was mentioned in the text, this “quasi”-degeneracy is lifted by taking into account either the spin-orbital or the Jahn–Teller effects.

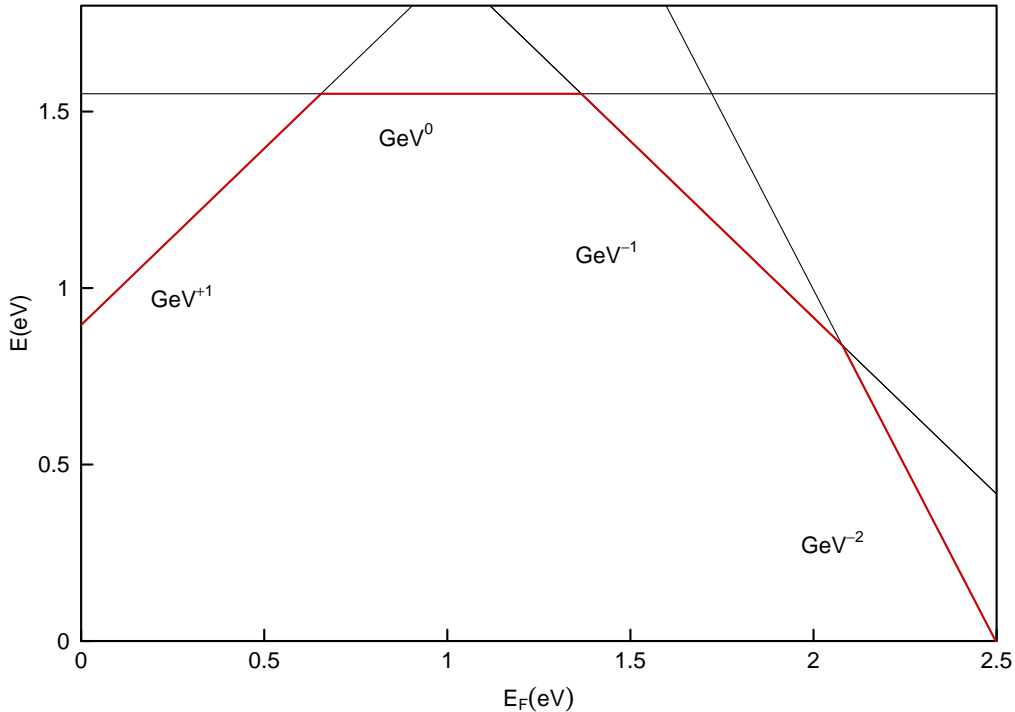


Figure 5: The calculated formation energy of the Ge–V defect as a function of the Fermi level position in the gap. The crossing points represent the charge transition levels. The chemical potential of Ge is taken from the cubic germanium

Calculation of defect formation energies demonstrates that four charged states $(+1, \dots, -2)$ are possible (see Fig. 5). It was found that $(\text{Ge-V})^{-1}$ and $(\text{Ge-V})^0$ are likely to exist in slightly p -doped diamond (which is quite realistic assumption, see discussion in the case of Si-V defects [S4]). Interestingly, changing of the charge state leads to a qualitative difference in the localization of the lower level (E_u) of the defect. In a negatively charged impurity it is located slightly above the valence band maximum. In this case, the excitation of electrons from this level rather than from the valence band maximum should lead to the observed photoluminescence and absorption effects.

6. Supplementary References

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