High pressure photoluminescence studies of diamond with GeV centers

S. G. Lyapin¹, A. A. Razgulov¹,², A. P. Novikov¹, E. A. Ekimov¹, M. V. Kondrin¹

¹L. F. Vereshchagin Institute for High Pressure Physics, RAS, Troitsk, Moscow, Russia
²Moscow Institute of Physics and Technology (State University), Dolgoprudny, Moscow, Russia
lyapins@hppi.troitsk.ru

PACS 33.50.Dq, 62.50-p DOI 10.17586/2220-8054-2018-9-1-67-69

We report low temperature (80 K) photoluminescence studies of microcrystalline diamond with germanium-vacancy (GeV) centers under hydrostatic pressure up to 6 GPa. Powders of Ge-doped diamond crystals were synthesized from hydrocarbons at high-pressures and high-temperatures. Due to the high quality of the samples, we were able to resolve the distinct quadruplet structure of the zero-phonon line (ZPL) of the GeV center already at 80 K and to trace it up to \( \sim 6 \) GPa. The pressure dependence of ZPL was found to be linear with the pressure coefficient \( dE/dP = 3.1 \) meV/GPa, which is nearly 3 times higher than that for the isomorphic SiV\(^-\) center. The experimentally observed pressure coefficients of GeV\(^-\), NV\(^-\) and NV\(^0\) centers are compared with results of \textit{ab-initio} DFT calculations, using Quantum ESPRESSO software package.

Keywords: diamond, color centers, high pressure, DAC.

Received: 19 June 2017
Revised: 19 September 2017

1. Introduction

The GeV colour center is a new recently discovered point defect in diamond [1–4] and a promising candidate for possible application as a single-photon emitter in quantum information processing, as luminescent marker in biology. Here we report pressure effect on the zero-phonon line (ZPL) in GeV\(^-\) centers under hydrostatic pressure up to 6 GPa. Knowledge of changes in the energy \( E \) of the zero-phonon line with hydrostatic stress is crucial in analysing temperature dependences and isotope shift of ZPL.

2. Experiment

Ge-doped diamond crystal powders were synthesized at high-pressures and high-temperatures from organic compound, naphthalene, mixed with Ge of natural isotopic composition [4]. Because of unintentional doping of diamond with nitrogen during synthesis, some of our samples contain nitrogen–vacancy defects (NV\(^-\) and NV\(^0\)) [4]. The presence of NV\(^0\) and NV\(^-\) -related peaks in the luminescence spectra of diamonds was revealed only upon cooling to 80 K, which indicates low concentration of such defects.

Photoluminescence (PL) spectra were recorded using the 488 nm Ar\(^+\) laser line for excitation and a triple-grating spectrometer (Princeton Instruments TriVista 555) with a liquid-nitrogen-cooled CCD detector. Diamond samples of 10 – 15 \( \mu \)m were placed in a diamond-anvil cell (DAC) along with ruby crystal, serving as a pressure sensor. Helium was used as pressure-transmitting medium. For low-temperature measurements, the DAC was put into a He cryostat (Oxford Instruments OptistatSXM) and an achromatic lens was used for focusing the laser beam and collecting the signal. The laser spot on the sample inside the cryostat was about 5 \( \mu \)m. Loading the pressure cell with the single diamond crystal containing both GeV and NV centers allowed us to study pressure effect on these three types of color centers in the same crystal and under the same conditions.

3. Results and discussion

Due to the high quality of the samples, we were able to resolve the distinct quadruplet structure of the zero-phonon line (ZPL) of the GeV center at all temperatures up to 80 K and to trace it up to 6.09 GPa – the highest pressure achieved in the experiment (Fig. 1). The pressure dependence of ZPL was found to be linear with the pressure coefficient \( dE/dP = 3.11 \) meV/GPa for the largest peak of the quadruplet (Fig. 2a, Table 1), which is nearly 3 times higher than that for the isomorphic SiV\(^-\) center [5]. The four-peak fine structure of ZPL is related to four optically allowed transitions between the split ground and excited states (Fig. 1b). Within the experimental error \( \pm 0.01 \) meV/GPa, the splitting of the ground state \( \Delta E_1 \) was insensitive to hydrostatic pressure, while the pressure coefficient of the splitting of the excited state \( \Delta E_2 \) was found to be 0.02 meV/GPa (Fig. 2b).
Fig. 1. a) High resolution PL spectrum revealing a quadruplet structure of ZPL of the GeV center at $T = 10\,\text{K}, P = 1\,\text{bar}$. b) Energy-level diagram with the split ground and excited states corresponding to four optical transitions presented at panel (a). c) Normalized PL spectra of diamond with GeV centers at various pressures at 80 K. d) Example of ZPL deconvolution into 4 Lorentz components, shown by dashed lines, reveals the quadruplet structure, corresponding to the energy-level diagram at panel (b) ($P = 6.09\,\text{GPa}, T = 80\,\text{K}$).

Fig. 2. a) Pressure dependence of peak positions of ZPL ($E_A$, $E_B$, $E_C$ and $E_D$, shown in Fig. 1). b) Pressure effect on the splitting of the excited ($E_C - E_A$, $E_D - E_B$) and the ground ($E_B - E_A$, $E_D - E_C$) levels of the GeV center.
TABLE 1. Experimental $\alpha = \frac{dE}{dP}$ and calculated $\alpha'$ pressure coefficients for ZPL in GeV$^-$, NV$^-$, NV$^0$ centers (present work) and SiV$^-$ centers (taken from Ref. [5]) (in meV/GPa)

|           | GeV$^-$ | SiV$^-$ | NV$^-$ | NV$^0$ |
|-----------|---------|---------|--------|--------|
| $\alpha$ (experiment) | 3.11 ± 0.03 | 1.04 ± 0.03 | 5.75 ± 0.07 | 2.18 ± 0.03 |
| $\alpha'$ (DFT)         | 3.08     | 1.5     | 6.5    | 5.3    |

The pressure dependence of ZPL for NV$^-$ and NV$^0$ centers was found to be linear with the coefficients 5.75 meV/GPa and 2.18 meV/GPa, correspondingly. Pressure coefficient for NV$^-$ peak is in good agreement with those obtained for diamond with only NV$^-$ centers [6, 7] as well as with data obtained for diamond with SiV and residual NV centers [5]. Because of the rather small investigated pressure range, we did not observe the nonlinearity of the pressure dependence of ZPL for NV$^-$ centers reported in Ref. [5].

The pressure coefficients for ZPL in GeV$^-$, NV$^-$, NV$^0$ centers (present work) and SiV$^-$ centers (taken from Ref. [5]) are compared in Table 1 with results of ab-initio DFT calculations with HSE06 nonlocal corrections, using Quantum ESPRESSO software package. In these calculations only redistribution of electron density with pressure increase was taken into account. Nevertheless, there is a reasonable agreement between calculated and experimentally observed pressure coefficients of GeV$^-$, SiV$^-$ and NV$^-$ centers. The only obvious deviation is the pressure coefficient of the neutral NV$^0$ center and in our opinion it might indicate more complicated structure of this center or stronger spin correlation effects, which were not considered in our calculations.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research, Projects 17-52-50075.

References

[1] Iwasaki T., Ishibashi F., et al. Germanium-Vacancy Single Color Centers in Diamond. Sci. Rep., 2015, 5, 12882.
[2] Palyanov Y.N., Kupriyanov I.N., Borzdyov Y.M., Surovtsev N.V. Germanium: a new catalyst for diamond synthesis and a new optically active impurity in diamond. Sci. Rep., 2015, 5, 14789.
[3] Ralchenko V.G., Sedov V.S., et al. Observation of the Ge-vacancy color center in microcrystalline diamond films. Bull. Lebedev Phys. Institute, 2015, 42 (6), P. 165–168.
[4] Ekimov E.A., Lyapin S.G., et al. Germanium-vacancy color center in isotopically enriched diamonds synthesized at high pressures. JETP Lett., 2015, 102 (11), P. 701–706.
[5] Lyapin S.G., Ilchev I.D., et al. Study of optical properties of the NV and SiV centers in diamond at high pressures. Book of Abstracts, 13th Intern. Conf. “Advanced Carbon Nanostructures”, 2017, St. Petersburg, Russia.
[6] Kobayashi M., Nisida Y. High-Pressure Effects on Photoluminescence Spectra of Color-Centers in Diamond. Jpn. J. Appl. Phys., 1993, 32, Suppl. 32-1, P. 279–281.
[7] Doherty M.W., Struzhkin V.V., et al. Electronic properties and metrology applications of the diamond NV$^-$ center under pressure. Phys. Rev. Lett., 2014, 112 (4), 047601.