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Study of optical properties of the NV and SiV centres in diamond at high pressures

S. G. Lyapin[1], I. D. Ilichev[1], A. P. Novikov[1], V. A. Davydov[1], V. N. Agafonov[2]

[1]L. F. Vereshchagin Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk, Moscow, Russia
[2]L. E. M. A., UMR CNRS-CEA 6157, University F. Rabelais, Tours, France

vdavydov@hppi.troitsk.ru

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We report photoluminescence studies of micro- and nano-sized diamonds with NV^0, NV^- and SiV^- centers under hydrostatic pressure up to 50 GPa. Diamonds have been obtained by high-pressure high-temperature (HPHT) treatment of metal-free growth systems based on mixtures of hydrocarbon, fluorocarbon, and silicone-containing organic compounds.

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1. Introduction

Color centers in diamond are considered now as an important basic element for different quantum-physical and biomedical applications. Although the properties of color centers in diamond have been studied very intensively for a long time, the pressure effect on photoluminescence is not well known. Knowledge of changes in the energy of the zero-phonon line (ZPL) with hydrostatic stress is crucial in analyzing temperature dependences [1,2], isotope shift [3] of ZPL. To our knowledge, the pressure coefficient was measured only for NV^- centers [4,5].

Here, we report pressure effect on zero-phonon line in SiV^-, NV^0 and NV^- centers under hydrostatic pressure up to 50 GPa.

2. Experimental

Homogeneous mixtures of naphthalene ($C_{10}H_8$), fluorographite ($CF_{1.1}$) and tetrakis(trimethylsilyl)silane ($C_{12}H_{36}Si_5$) were used as starting materials for synthesis of diamond with optically active SiV^-, NV^0 and NV^- point defects. The synthesis was performed in a high-pressure apparatus of “Toroid” type [6]. Cylindrical samples of the initial mixtures (4 mm diameter and 5 mm height) obtained by cold pressing were put into graphite containers which were placed in the high-pressure apparatus. The experimental procedure consisted in loading the apparatus up to 8 GPa, heating up to the desired temperature ($\sim$ 1200 °C) and short isothermal exposure under constant load for 5 – 10 s. The SEM images of the obtained products, which are mixtures of nano- and submicrometer-size fraction of diamond, show that the formation of diamond occurs with virtually 100 % yield.

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, representing distinct agglomerates of micro- and nanoscale diamonds, 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 measurements at room temperature, a 50× objective (NA = 0.50) of a confocal microscope (Olympus BX51) was used to focus the laser beam and to collect the PL signal. To perform measurements at 80 K, 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 $\sim 5\ \mu$m.

3. Results and discussion

Figure 1 shows typical photoluminescence spectra collected on diamonds doped with silicon of natural isotope composition. Because of unintentional doping of diamond with nitrogen occurred during synthesis, some of our samples contain nitrogen-vacancy defects (neutral NV^0 and negatively charged NV^-) detectable already at room temperature 296 K [6]. Two types of diamonds were used in pressure experiments i) with high concentration SiV^- centers in order to track ZPL from SiV^- centers; ii) with low concentration SiV^- centers to allow detection of ZPL from NV centers. We were able to follow ZPL from SiV^- and NV^0 centers up to $\sim$ 52 GPa (the maximum pressure achieved in our experiment). However, ZPL from NV^0 centers became undetectable above $\sim$ 40 GPa.

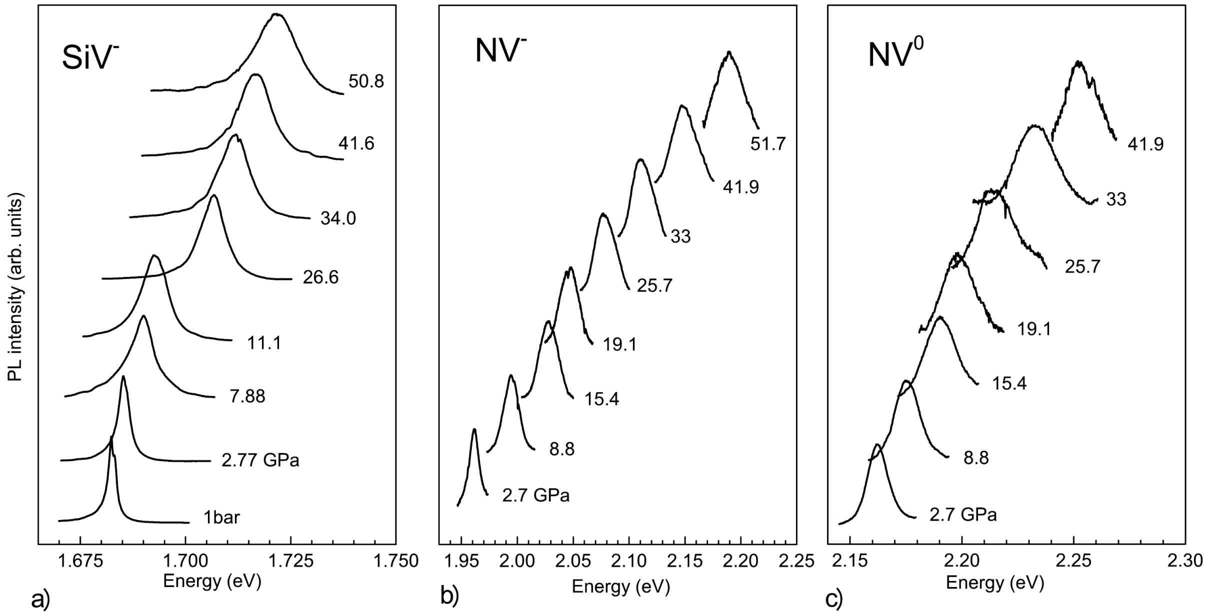

FIG. 1. Normalized PL spectra of diamond with SiV$^-$ (a), NV$^-$ (b), NV^0 (c) centres at various pressures at 80 K. The background for spectra in panel (b) and (c) was subtracted for clarity

Pressure dependences of ZPL of negatively charged NV$^-$ and SiV$^-$ centers at 80 and 296 K were approximated by the second order polynomial equation: $E(P) = E_0 + \alpha P + \beta P^2$, while that of the neutral NV^0 center was found to be linear with rather good precision (Fig. 2, Table 1). If we use equation of state for diamond [7] to replot ZPL position versus natural logarithm of lattice constant of diamond ($\ln[a(P)/a_0]$), the nonlinear dependence of peak position for negatively charged NV and SiV centers remains.

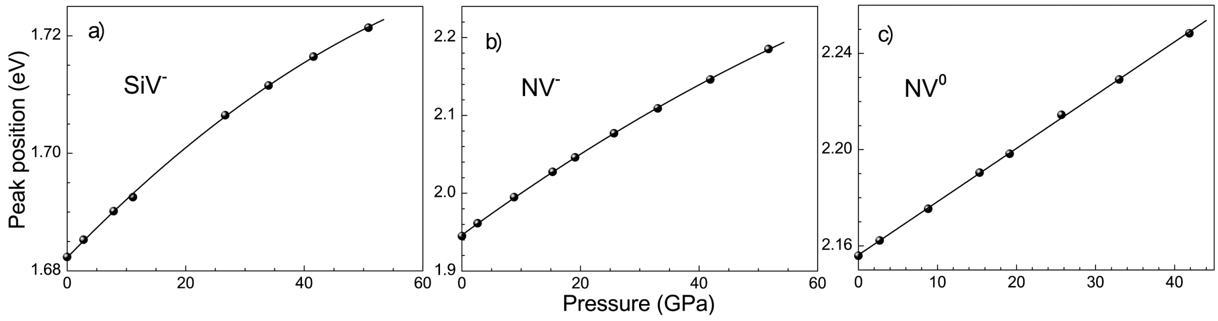

FIG. 2. Pressure dependence of ZPL in SiV$^-$ (a), NV$^-$ (b), NV^0 (c) centres at 80 K

The pressure coefficients α for NV$^-$ centers are in good agreement with those obtained at 77 K [4] and at room temperature [5] and they are reasonably close to the pressure coefficients of the direct and indirect gaps in diamond [8,9]. The obtained data show that the effect of pressure on the position of zero-phonon lines most sharply manifested in the case NV$^-$ centers, for which the α coefficient value at 296 K is equal to 5.81 meV/GPa. In the case of the SiV$^-$ center, the α coefficient is equal to 1.09 meV/GPa, which is 5-fold less than the previous value. The α coefficient value for neutral NV centers is 2.14 meV/GPa, meaning it has an intermediate value between the corresponding values of negatively charged NV$^-$ and SiV$^-$ centers. Significant difference in the α coefficient values of negatively charged NV$^-$ and SiV$^-$ centers is associated, obviously, with the different structures for these two types of diamond lattice defects.

TABLE 1. Pressure coefficients for ZPL in SiV^-, NV^- and NV^0 centres at 296 and 80 K

$E(P) = E_0 + \alpha \cdot P + \beta \cdot P^2$						
	296 K			80 K		
Center	E_0 (eV)	α (meV/GPa)	$\beta \cdot 10^{-3}$ (meV/GPa^2)	E_0 (eV)	α (meV/GPa)	$\beta \cdot 10^{-3}$ (meV/GPa^2)
SiV^-	1.680	1.09	−5.7	1.682	1.04	−5.3
NV^-	1.943	5.81	−25	1.946	5.57	−19
NV^0	2.156	2.14	0	2.156	2.21	0

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References

[1] Neu E., Hepp C., et al. Low-temperature investigations of single silicon vacancy colour centres in diamond. *New J. Physics*, 2013, **15** (4), 043005.

[2] Jahnke K.D., Sipahigil A., et al. Electronphonon processes of the siliconvacancy centre in diamond. *New J. Physics*, 2015, **17**, 043011.

[3] Collins A.T., Davies G., Kanda H., Woods G.S. Spectroscopic Studies of C-13 Synthetic Diamond. *J. Physics C: Solid State Physics*, 1988, **21** (8), P. 1363–1376.

[4] Kobayashi M., Nisida Y. High-Pressure Effects on Photoluminescence Spectra of Color-Centers in Diamond. *Jpn. J. Appl. Phys.*, 1993, **32**, P. 279–281.

[5] 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.

[6] Davydov V.A., Rakhmanina A.V., et al. Production of nano- and microdiamonds with Si–V and N–V luminescent centers at high pressures in systems based on mixtures of hydrocarbon and fluorocarbon compounds. *JETP Lett.*, 2014, **99** (10), P. 585–589.

[7] Occelli F., Loubeyre P., Letoullec R. Properties of diamond under hydrostatic pressures up to 140 GPa. *Nature Mater.*, 2003, **2** (3), P. 151–154.

[8] Wei S.H., Zunger A. Predicted band-gap pressure coefficients of all diamond and zinc-blende semiconductors: Chemical trends. *Phys. Rev. B*, 1999, **60** (8), P. 5404–5411.

[9] Onodera A., Hasegawa M., et al. Pressure-Dependence of the Optical-Absorption Edge of Diamond. *Phys. Rev. B*, 1991, **44** (22), P. 12176–12179.