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EPR of phosphorus in diamond crystals. An influence of nitrogen impurity, HTHP treatment and high phosphorus concentration

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Semiconductor diamond

Diamond is a promising material for electronic devices, because its radiation and thermal hardness is greater than that of silicon. So such devices can be used in space and nuclear technology. Also diamond has very high thermal conductivity, so semiconductor diamond can be used in high power electronics.

Diamond has wide band gap (5.5eV). It is known that diamond can easily be doped with boron atoms producing p-type conductivity (defect state is 0.37eV above the top of the valence band). Since nitrogen possesses one more electron than carbon, it could be considered as a potential donor, however, its level in the forbidden band is too deep (1.7eV below the bottom of conduction band). In present times, the primary focus is directed toward the creation of n-type conductivity in the diamond via doping of phosphorus (0.6eV below the bottom of conduction band). But most of the works on this topic are empirical, so the description of phosphorus incorporation into the diamond is incomplete.

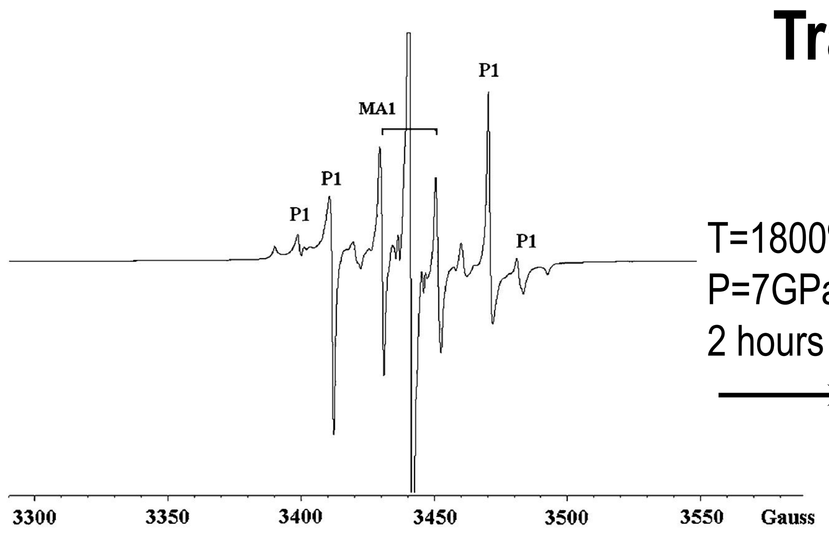
Samples

Weighted portions of the diamond crystals were synthesized via the high-pressure high-temperature method (using split-sphere-type multianvil apparatus BARS)

- in the P-C system with different P concentrations
- in the temperature range 1600-1800°C
- in the pressure range 6.3-7GPa
- without seed crystals (crystals are ~100μm in size)

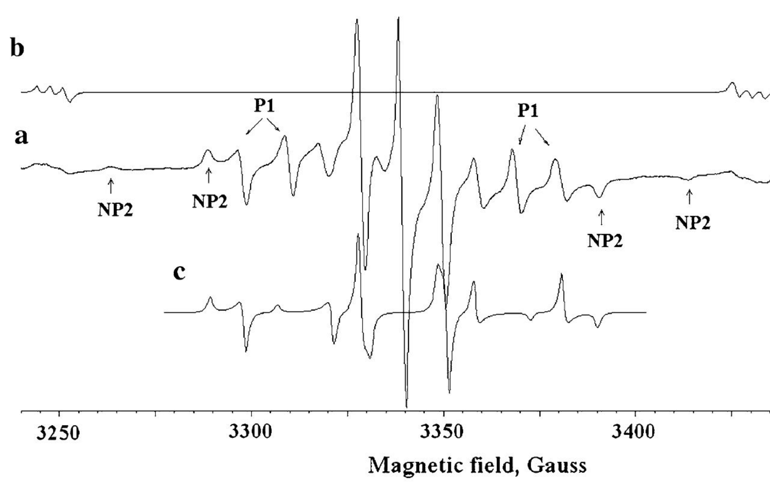
The high-pressure annealing of the phosphorus containing diamonds was also performed by BARS.
Samples have been obtained by Y.N. Palyanov, I.N. Kupriyanov (IGM SB RAS).

Transformation of phosphorus-related centers in HPHT synthetic diamonds



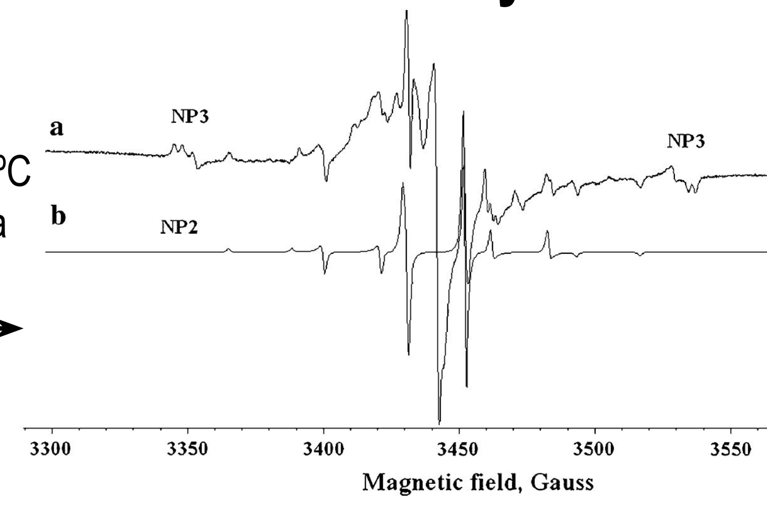
X-band EPR spectrum of synthetic microdiamonds grown at 1600°C in the P–C system

T=1800°C
P=7GPa
2 hours



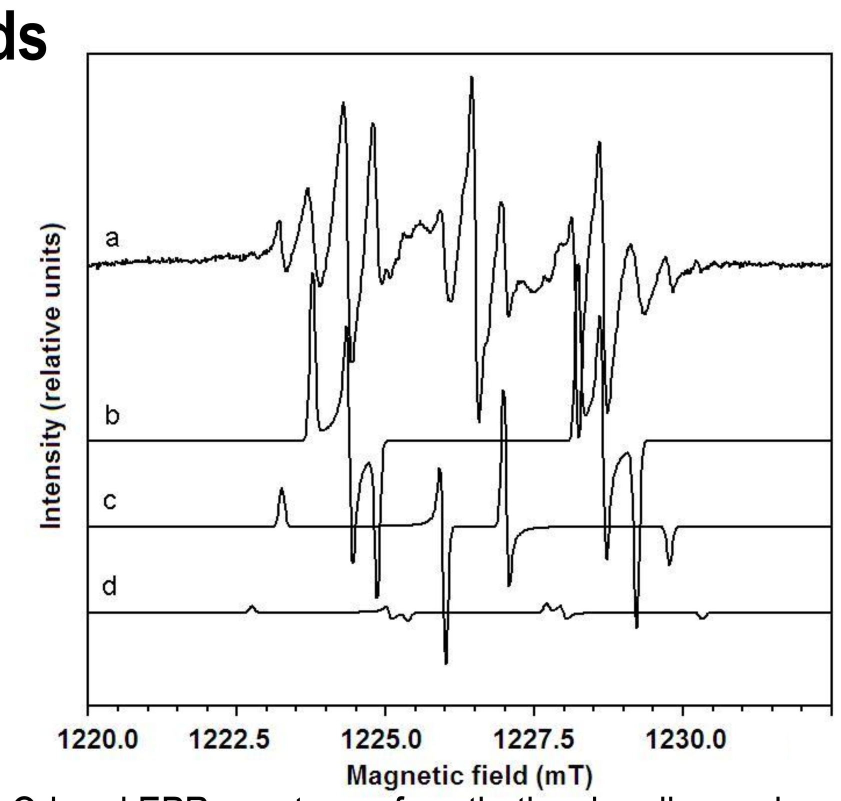
X-band EPR spectra of synthetic microdiamonds grown at 1600°C after annealing at 1800°C **a** experimental spectrum, **b** simulated spectrum of the NP3 center, **c** simulated spectrum of the NIRIM8 (NP1) center

T=2000°C
P=7GPa
2 hours

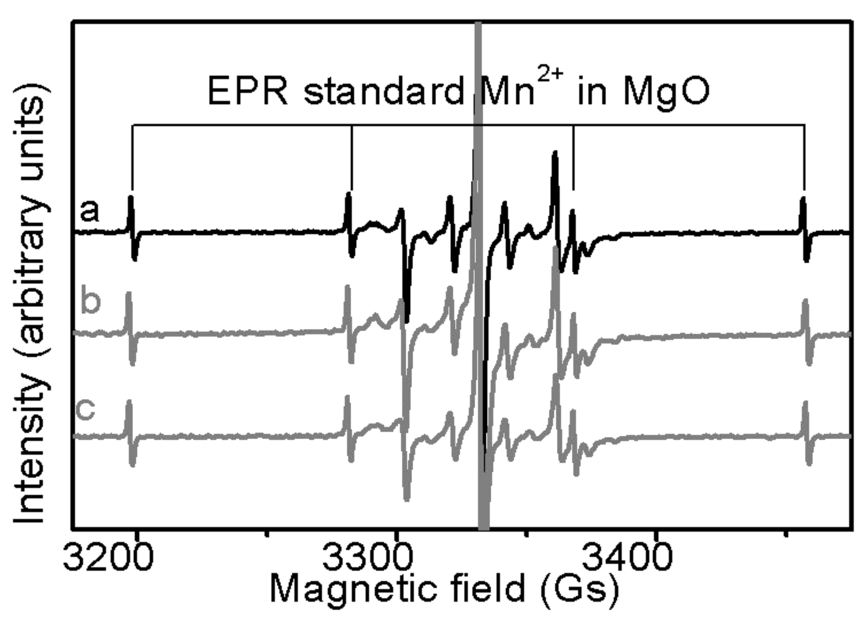


X-band EPR spectrum of synthetic microdiamonds grown at 1600°C after annealing at 2000°C **a** experimental spectrum, **b** simulated spectrum of the NP2 center

T=2300°C
P=7GPa
10 min



Q-band EPR spectrum of synthetic microdiamonds grown at 1600°C after annealing at 2300°C after X-ray irradiation **a** experimental spectrum, **b** simulated spectrum of the NP4 center, **c** simulated spectrum of the NP5 center, **d** simulated spectrum of the NP6 center

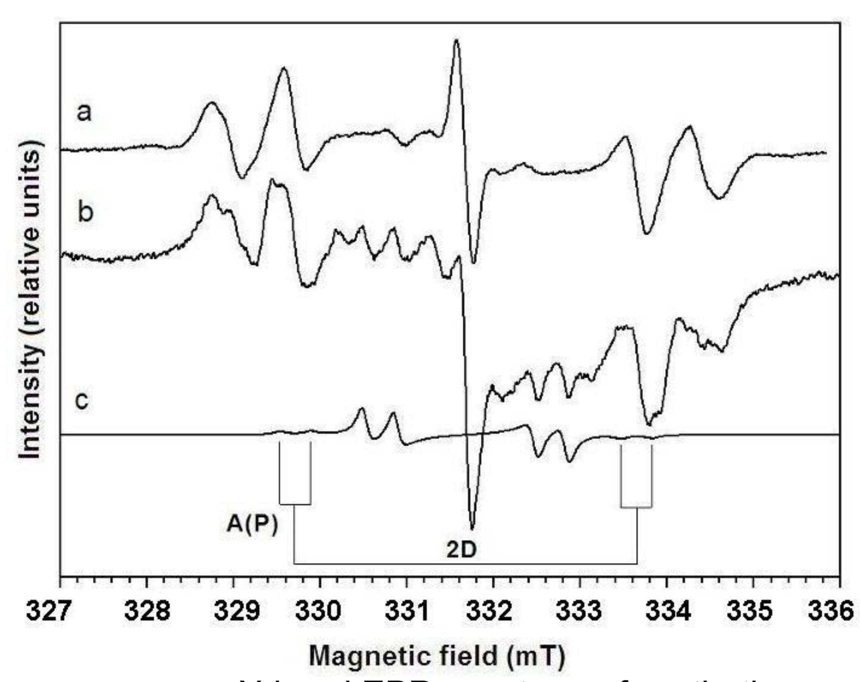


X-band EPR spectrum of synthetic microdiamonds grown at 1700°C **a** experimental spectrum before electron irradiation, **b** experimental spectrum after electron irradiation (3.5MeV, 5x10^{17} e/cm^2) **c** after subsequent heat treatment at 700°C during 2h

In diamonds with low concentration of phosphorus (~100 ppm) series of nitrogen-phosphorus defects has been revealed. In the crystals grown at 1600°C and 7GPa isolated substitutional nitrogen (P1) and phosphorus (MA1) atoms are observed by EPR. First heat treatment at 1800°C and 7GPa results in the formation of NP1 center containing nitrogen and phosphorous atoms separated by two carbon atoms. If the annealing temperature is increased to 2000°C NP1 center transforms into a pair of nitrogen-phosphorus atoms separated by one carbon atom (NP2 center) and then into a close pair of nitrogen-phosphorus atoms (NP3 center). Further annealing at the temperature of 2300°C leads to the lattice relaxation of the structures of nitrogen-phosphorus centers NP1 - NP3, paramagnetic centers NP4 - NP6 with semivacancy structures formed. NP5 and NP6 centers emerge after the crystals undergo X-ray irradiation. NP4, NP5 and NP6 are proposed to differ in different position of nitrogen atom in the structure of the defect.

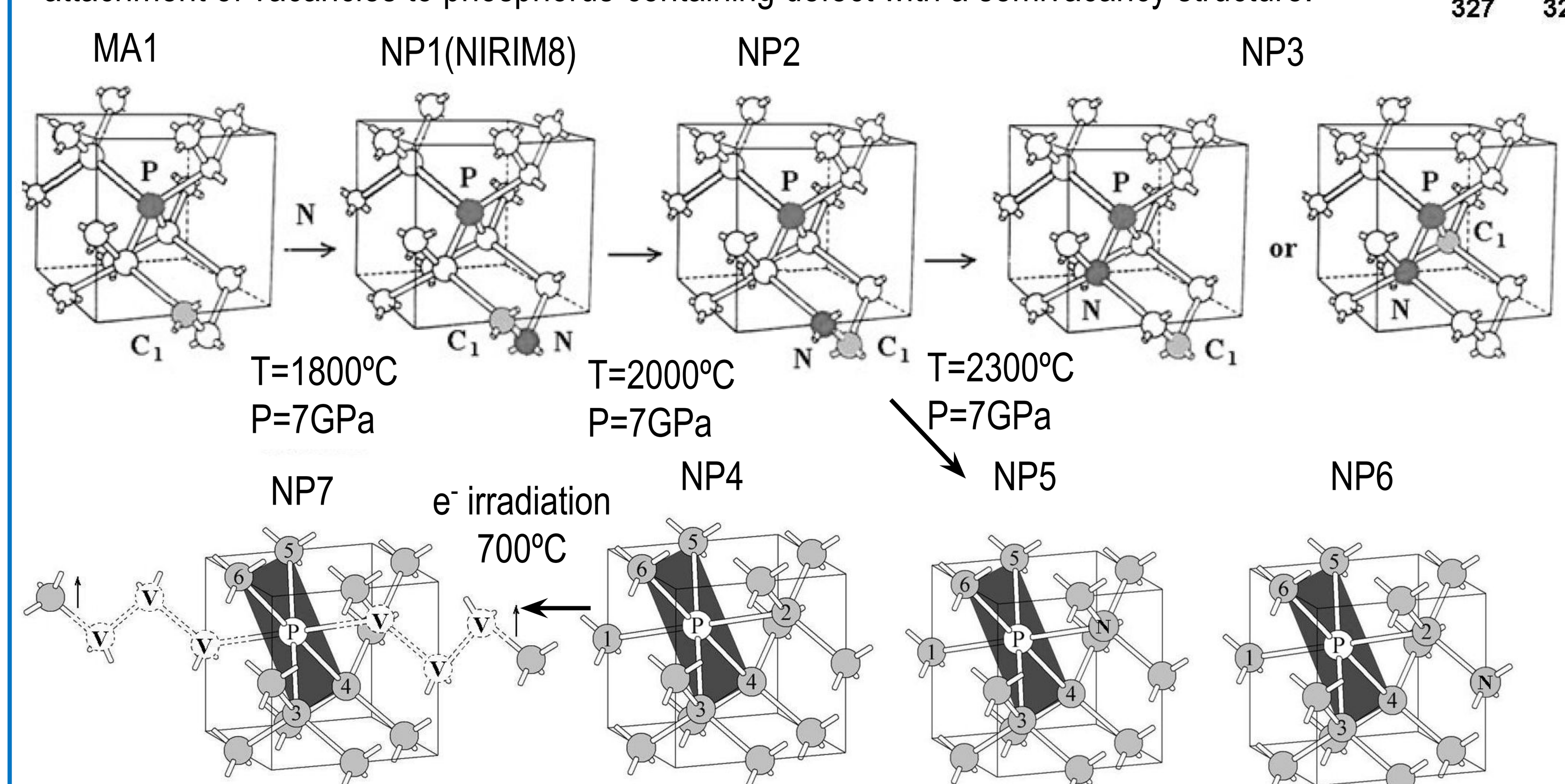
Experiments on electron irradiation and subsequent 700°C annealing of diamonds containing MA1, NP1 – NP3 centers have shown that substitutional nitrogen is a charge compensator of these centers. The iirradiation leads to the decrease of the spectra intensities of phosphorus containing centers and the little increase of the spectra intensity of substitutional nitrogen P1. So the experiment with electron irradiation has given the direct evidence of N^- charge state of nitrogen in diamond. Experiments on electron irradiation of the 2300°C annealed sample with subsequent 700°C annealing give new center NP7, it proposed to have the structure of eight-vacancy chain with a phosphorus atom in the center. NP7 is thought to be formed by attachment of vacancies to phosphorus-containing defect with a semivacancy structure.

e$^-$(3.5MeV, 5x10^{17} e/cm^2) + 700°C, 2hours



X-band EPR spectrum of synthetic microdiamonds grown at 1600°C after annealing at 2300°C **a** experimental spectrum before electron irradiation, **b** experimental spectrum after electron irradiation and heat treatment at 700°C during 2 h, **c** simulated spectrum of the NP7 center

Center	S, g-values	Spin Hamiltonian parameters (Gs)
P1	S=½, g=2.0025	$A(N)_{\parallel}$=40.8, $A(N)_{\perp}$=29.2 $A(C_1)_{\parallel}$=121.6, $A(C_1)_{\perp}$=139.2
MA1	S=½, g=2.0025	$A(P)_{\parallel}$=23.2, $A(P)_{\perp}$=19.6 $A(C_1)_{\parallel}$=181.3, $A(C_1)_{\perp}$=139.2
NIRIM8 (NP1)	S=½, g_1=2.00243, g_2=2.0028, g_3=2.0026	$A(P)_1$=20.8, $A(P)_2$=20.2, $A(P)_3$=21.8 $A(N)_1$=40.8, $A(N)_2$=31.0, $A(N)_3$=30.0
NP2	S=½, g=2.0025	$A(P)_{\parallel}$=23.4, $A(P)_{\perp}$=20.9 $A(N)_{\parallel}$=64.2, $A(N)_{\perp}$=30.9
NP3	S=½, g=2.0025	$A(P)_{\parallel}$=174.8, $A(P)_{\perp}$=182.3 $A(N)_{\parallel}$=1.0, $A(N)_{\perp}$=3.3
NP4	S=½, g_1=2.0009, g_2=2.0012, g_3=2.00047	$A(P)_1$=54.56, $A(P)_2$=38.38, $A(P)_3$=38.0
NP5	S=½, $g_{\parallel}$=2.00087, $g_{\perp}$=2.0009	$A(P)_{\parallel}$=65.22, $A(P)_{\perp}$=10.24
NP6	S=½, g_1=2.00085, g_2=g_3=2.00083	$A(P)_1$=75.85, $A(P)_2$=29.42, $A(P)_3$=23.28
NP7	S=1, g=2.0012	D=19.7, E=0, $A(P)$=3.6
NP8	S=½, $g_{\parallel}$=2.0044, $g_{\perp}$=2.0011	$A(P)_{\parallel}$=56.3, $A(P)_{\perp}$=31.5
NP9	S=½, g_1=2.0026, g_2=2.0057, g_3=2.0026	$A(P_1)_1$=96, $A(P_1)_2$=91, $A(P_1)_3$=134 $A(P_2)_1$=20, $A(P_2)_2$=20, $A(P_2)_3$=16
NP10	S=½, $g_{\parallel}$=2.0016, $g_{\perp}$=2.0015	$A(P)_{\parallel}$=59.6, $A(P)_{\perp}$=38.8

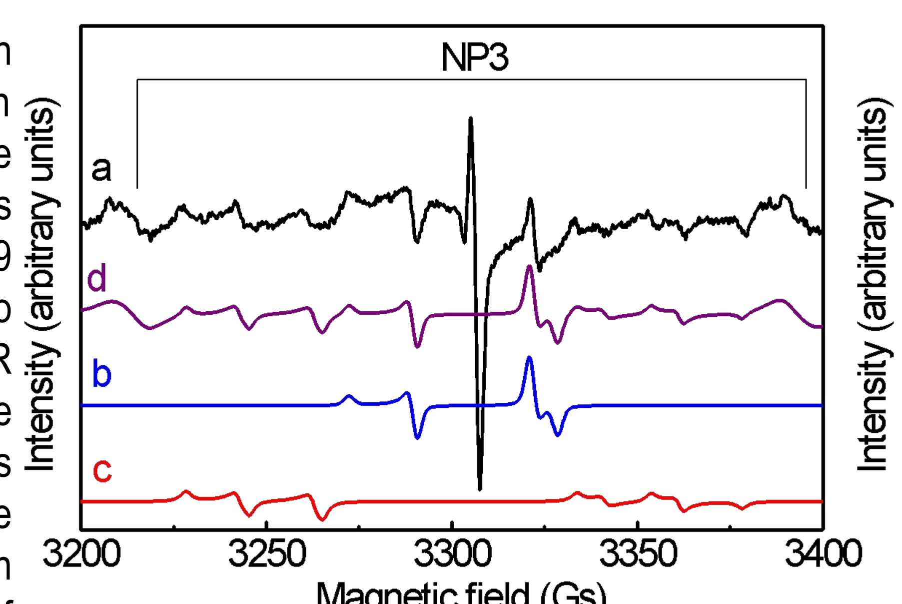


1. Nadolinny, V.A., Pal'yanov, Yu.N., Kalinin, A.A., Kupriyanov, I.N., Veber, S.L., Newton, M.J. Transformation of As-Grown Phosphorus-Related Centers in HPHT Treated Synthetic Diamonds //Appl. Magn. Reson. – 2011. – Vol. 41. – P. 371-382.
2. Komarovskikh, A., Nadolinny, V., Pal'yanov Y., Kupriyanov, I, Sokol, A. EPR of new phosphorus-containing centers in synthetic diamonds //Phys. Status Solidi A. – 2013. – Vol. 210. – P. 2078-2082.

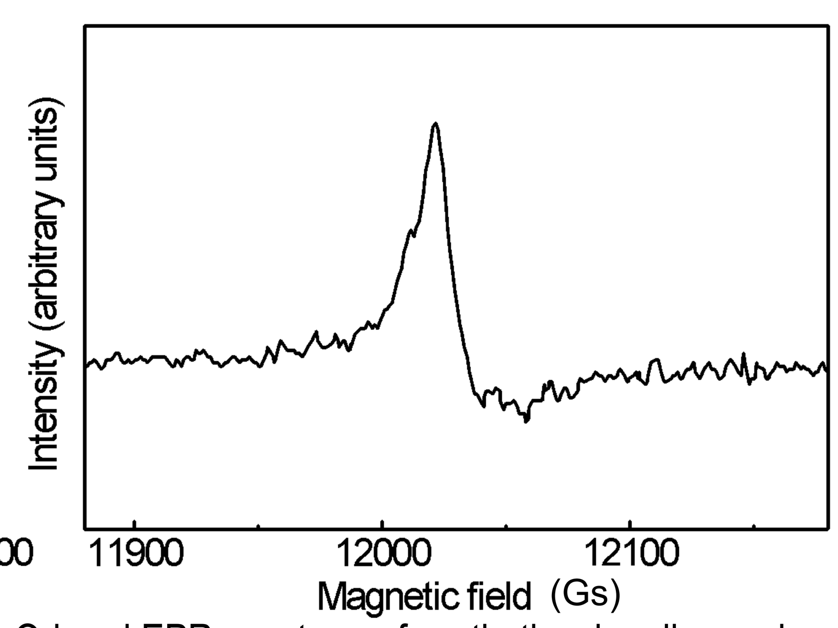
EPR of synthetic diamonds heavily doped with phosphorus

Diamonds grown in the medium with high concentration of phosphorus in the presence of Al at 1600°C and 6.3GPa demonstrate no visible lines in EPR spectra at room temperature. But at 77K in the EPR spectrum of the studied microcrystals new spectra NP8 and NP9 are observed besides NP3 spectrum. NP8 demonstrates HFS of one phosphorus atom, NP9 demonstrates HFS of two phosphorus atoms. Reduction in temperature to 40 K leads to the saturation of the NP3, NP8 and NP9, a new EPR spectrum associated with conductivity electrons in form of Dyson line appears with g-factor g=2.00(1). So, in part of the microcrystals nitrogen-phosphorus defects are observed. In other microcrystals we detect the formation of phosphorus pairs in adjacent carbon positions. In microcrystals with high phosphorus impurity concentration degeneration of the levels into zone near the conduction band takes place.

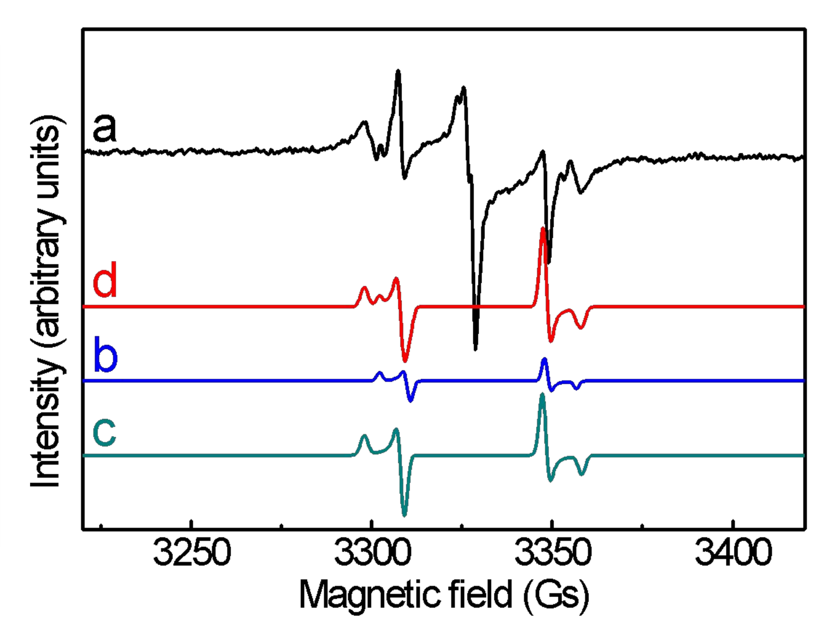
Annealing of as grown diamond crystals at temperature of 2000°C leads to the disappearance of the NP3, NP8 and NP9 spectra and combination of NP4 and new spectrum NP10 is observed. Spin Hamiltonian parameters of NP10 is close to them of NP4, its structure is discussed.



X-band EPR spectrum of synthetic microdiamonds grown at 1600°C in C-P medium with high concentration of phosphorus (77K) **a** experimental spectrum, **b** simulated spectrum NP8, **c** simulated spectrum NP9, **d** sum of simulated NP3, NP8 and NP9



Q-band EPR spectrum of synthetic microdiamonds grown at 1600°C in C-P medium with high concentration of phosphorus (40K), A/B=5.7, ΔH=19.31Gs



X-band EPR spectrum of synthetic microdiamonds grown at 1600°C in C-P medium with high concentration of phosphorus after annealing at 2000°C (77K) **a** experimental spectrum, **b** simulated spectrum NP4, **c** simulated spectrum NP10, **d** sum of simulated NP4 and NP10