Paramagnetic defects and exchange coupled spins in pristine ultrananocrystalline diamonds

V.Yu. Osipov\textsuperscript{a,c,*}, A.I. Shames\textsuperscript{b}, T. Enoki\textsuperscript{c}, K. Takai\textsuperscript{c}, M.V. Baidakova\textsuperscript{a}, A.Ya. Vul’\textsuperscript{a}

\textsuperscript{a} Ioffe Physico-Technical Institute, Polytechnicheskaya 26, St.Petersburg 194021, Russia
\textsuperscript{b} Department of Physics, Ben-Gurion University of the Negev; P.O. Box 653, 84 105 Be’er-Sheva, Israel
\textsuperscript{c} Department of Chemistry, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo 152-8551, Japan

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Abstract

Electron paramagnetic resonance (EPR) and magnetic susceptibility measurements were done on nanodiamond samples fabricated by the detonation method and purified by acids. Comprehensive acid treatment leads to the reduction of EPR signals of magnetic impurities and revealing two weak and narrow EPR lines with $g_1 = 4.26$, $\Delta H_{pp} = 2.9$ mT and $g_2 = 4.00$, $\Delta H_{pp} = 1.4$ mT at $T = 4$ K, separated by the distance of 10.4 mT. The origin of this new doublet EPR signal observed in the well purified sample is discussed. The magnetic susceptibility behavior and doublet EPR signal ($g \sim 4$) suggest the weak antiferromagnetically exchange coupling of $S = 1/2$ paramagnetic defects as well as the presence of isolated dimers with $S = 1$.

1. Introduction

Nanodiamond (ND) produced by the detonation method is one of the new kinds of nanocarbons that have been intensively studied since the late eighties [1]. An unusual feature of detonation ND is a sharp distribution in size, with the size of most particles varying between 4 and 5 nm [2,3]. Every ND particle consists of a diamond sp\textsuperscript{3}-core of about 5 nm diameter and a sp\textsuperscript{2}-hybridized (graphene) carbon-shell around the core. The shell structure and its thickness depend on the detonation conditions and chemical treatments of the non-diamond forms of carbon on the ND surface [4]. Nitric acid treatment at elevated temperatures (200–230 °C) in autoclave together with subsequent hydrothermal treatment in supercritical water ($P = 100$ MPa, $T = 650$ °C) results in dissolution of graphitic-like shell covering the diamond core. It allows fabrication of ND crystals with graphitic-free and even partly hydrogen-terminated surfaces [5]. ND particles with graphitic-free surface have octahedral or cubo-octahedral shapes in the case they are bound by eight (111) or additionally by six (100) crystal planes respectively [6].

Preceding magnetic resonance studies revealed presence of a very intensive singlet EPR signal with $g = 2.0027$ and line width $\Delta H_{pp} \sim 0.8–0.9$ mT, associated with uncoupled spins localized at broken carbon–carbon bonds; concentrations of these paramagnetic centers were found to be $\sim 10^{19}$ spin/g [7]. Parameters of the EPR signal observed are most close to those of the EPR signal originated from broken bonds on the diamond surface ($g = 2.0027$, $\Delta H_{pp} = 0.55$ mT) [8]. Further EPR studies [9–13] of ND, obtained by both so-called wet and dry detonation synthesis, were targeted to the origin of paramagnetic centers in ND as well as tracking nanodiamond to nanographite conversion due to the heat treatment in Ar atmosphere. These studies just confirmed the aforementioned EPR parameters, which were found to be practically independent (except of $\Delta H_{pp}$) [11] on the fabrication technique. The most comprehensive EPR and high-resolution transmission electron microscopy (HRTEM) study of purified...
detonation diamonds is reported in Ref. [12]. It was shown [14] that EPR is a powerful tool for the control of paramagnetic and ferromagnetic impurities during the processes of ND purification.

2. Sample preparation and magnetic studies

2.1. Samples and chemical treatment

The initial sample #1 used for this research was a commercially available nanodiamond powder produced by means of the following industrial technology: at first the starting material of explosion produced carbon (‘detonation carbon’) was obtained by detonation of 60/40 mixture of TNT/hexogen in a gaseous CO₂ medium (so-called ‘dry synthesis’), in a commercial setup. Then, nanodiamond powder (with the mean particle size 4–5 nm) was chemically extracted and separated from non-diamond forms of carbon and metallic impurities contained in the detonation soot by treating in 50% aqueous nitric acid at temperature of about 230 °C and elevated pressure in an autoclave. Nevertheless, nanodiamond powder (#1) cleaned primarily in the chemical plant by this method still contained remarkable amount of metallic impurities, mainly iron(III)-ion containing complexes. Usually traces of such metals as Fe, Cr and Ti appear in the composition of nanodiamond powder because the strong walls of detonation chamber and autoclave are made from stainless steel. The fact that iron is a main transition-metal impurity in commercially available nanodiamonds is well known [15] and proved by appearance of multiple diffraction peaks of magnetite (FeFe₂O₄) in the XRD spectra of the detonation carbon and nanodiamonds annealed at a temperature more than 1000 °C [12].

To avoid the possible effect of magnetic 3d-transition-metal impurities on the subsequent experimental magnetic measurements and their results, the laboratory amount of nanodiamond powder (1–2 g) was subjected to repeated chemical treatments in 38% hydrochloric acid (5 treatments at forced-circulation boiling) and then washed in boiling distilled water (5 times) before the measurements. This nearly totally removed the transition-metal impurities usually present in commercial detonation nanodiamonds. Then the obtained powder (#2) was dried in vacuum condition at room temperature.

Finishing hydrothermal treatment (HyTT) was carried out for further final purification nanodiamond particles from graphitic-like coverage, hydrogen termination of the ND surface and fresh diamond surface stabilization. The ND powder (about 50–70 mg) was sealed in a gold capsule filled with distilled water in a molar ratio of ND:H₂O=1:3 and treated at 650 °C and 100 MPa for 15–30 h. In this process, the dissolution of the carbon external transient layer (sp²-hybridized carbon-shell and interface defective sp³-region) covering the crystalline ND core and its partial or even complete removal take place. Thus, the graphitic shell and the most defective sites of the interface sp²/sp³ structure are etched selectively under the HyTT condition. Then the HyTT nanodiamond samples (#3) obtained were dried in vacuum condition at room temperature.

2.2. Magnetic susceptibility measurements

The magnetic susceptibility and magnetization measurements of acid-treated ND were carried out with a Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design Co., MPMS-5) in the temperature range of 1.9–380 K in magnetic fields up to 5.5 T in vacuum. The samples for the SQUID measurements were packed into a capsules made from a thin aluminum or copper foil and vacuum-sealed in quartz tubes after the treatment at 400 °C for 4.5–5.5 h at the vacuum level of about (1.2–2.0)×10⁻⁶ Torr.

Subsequent study of the magnetic properties on the acid-treated ND sample #2, done using SQUID magnetometer, shows that spin paramagnetism in acid-treated ND #2 is associated only with the localized defects with S=1/2. The magnetization (M–H) curve measured at the lowest temperature available T=1.9 K in magnetic fields H up to 5.5 T, may be represented as the sum of the temperature-independent linear (M–H) curve with a negative slope $\chi_o \times H$ (here $\chi_o$ is a temperature-independent term in the magnetic susceptibility $\chi_o=-(0.35\times10^{-6} \text{emu/g}$ which is very close to the value of core diamagnetic susceptibility of the carbon atoms) and the characteristic curve with a positive contribution of $S=1/2$ and a saturating trend in the high magnetic field. The latter being well-fitted to the so-called Brillouin curve with a $S=1/2$ yields an effective (i.e. observed in this experiment) concentration of local magnetic moments ($S=1/2$) of 4.19×10¹⁹ spins/g. No contribution to the magnetization curve due to transition-metal ions impurities (with spins S>1/2 , i.e. S=1, 3/2 , 2, 5/2), in contrast with that observed in worse purified ND #1, is observed.

The acid-treated NDs #2 were also studied by means of temperature-dependent magnetic susceptibility $\chi=\chi(T)$ measurements within the whole temperature range. The temperature dependence of $\chi$ for the sample #2 is shown in the inset in Fig. 1 in the coordinate scale $1/(\chi-\chi_o)$ vs. $T$. It is found that in the acid-treated ND #2 the temperature dependence of magnetic susceptibility follows well or roughly well the Curie law, where the localized spins originate from dangling C–C bonds of sp² sites located mainly in the interior of the nanocrystals and also from the stable free radicals located on the surface/or within the surface layer of the ND crystallite. Here we suppose that the susceptibility may be represented as a combination of the temperature-dependent Curie–Weiss term $C/(T-\Theta)$ and the temperature-independent negative term $\chi_o$, where $C$ is a Curie constant and $\Theta$ is a Weiss temperature.

The inverse slope of the curve plotted in the inset in Fig. 1 provides data on the absolute value of localized spin concentration in the system. The concentration of the intrinsic localized spins $N_s$ in acid-treated ND #2, obtained from the inverse of the curve’s slope (or the Curie constant), is found to be $6.3\times10^{19}$ spins/g and exceeds the effective concentration of localized magnetic moments determined from the magnetization $M–H$ curve at the lowest temperature $T=1.9$ K. This value $N_s$ (assuming the average diameter and the density of ND particles equal to 5.0 nm and the density of bulk diamond 3.52 g/cm³, respectively), is found to be about 13–14 spins per nanoparticle. These are the same spins directly responsible for
the appearance of the main EPR signal ($g\sim 2$) in nanodiamonds (see Section 2.3).

Such a small number of localized spins, as compared with the total number of the (111) surface carbon atoms in a particle of octahedral shape with up-standing ($\uparrow$) bonds (ca. 1500), indicate that the surface bonds of a diamond core are almost totally terminated and radical-like paramagnetic centers observed are due to the point-like structural defects in/on the diamond core [12–14].

In order to produce any certain conclusion about the interaction between the spins in the system the $\chi$ vs. $T$ dependence was plotted in the coordinates of $(\chi-\chi_0)\times T$ vs. $T$ (Fig. 1). The downward turn on this curve in the low-temperature region $T<50$ K points out the presence of a weak antiferromagnetic (AFM) interaction between the unpaired electron spins. For this magnetic coupling the Weiss temperature was found to be $\Theta=-1.12$ K. It means that the exchange coupling between the localized spins is quite weak, but nevertheless noticeable, and occurs probably due to typical through-space interactions between the uncoupled spins. Thus, magnetic phenomena in pristine well purified nanodiamonds are caused by localized spins with $S=1/2$, most part of them are weakly antiferromagnetically coupled.

2.3. Electron paramagnetically coupled

Acid-purified nanodiamond samples were also investigated by means of electron paramagnetic resonance (EPR). CW EPR spectra were obtained using commercial X-band ($\nu=9–9.4$ GHz) EPR spectrometers within the temperature range 4–600 K. In order to register correctly both strong radical-like signals and weak signals from traces of impurities the following parameters were used (depending on the signal type): microwave power 0.2–20 mW, modulation 0.5–1 mT, amount of powder in quartz EPR tube of about 40 mg. Three samples were studied: the first one — purified by only nitric acid (#1), the second one — the same as #1 with the subsequent treatment by 38% hydrochloric acid (#2) and the third one — the same as #2 with the following hydrothermal treatment in supercritical water at $P=100$ MPa, $T=650$ °C (#3).

EPR spectrum of sample #1 (not shown here) consists of two lines: the intensive narrow ($\Delta H_{\text{pp}}=0.85$ mT) line with $g=2.0026$, corresponding to the spin concentration of 10–14 spins per particle and the weak broad ($\Delta H_{\text{pp}}=30$ mT) one, located in a half-field region ($g=4.28\pm0.01$). The narrow line originates from the existence of dangling C–C bonds located inside the diamond core and/or within the surface layers of nanodiamond particle (see Refs. [11,12,14]). The broad line may be attributed to transition-metal ions’ impurities, mainly rhombically distorted Fe$^{3+}$−containing complexes located in the vicinity of the nanodiamonds. This fact is in a good agreement with magnetic susceptibility data at $T=1.9$ K where the magnetization curve of sample #1 indicates significant contribution of spins with $S=1/2$. The most convincing argument in favor of attributing the narrow ESR signal to the structural defects in/on the nanodiamond core comes from the independence of width of narrow ESR line of the gas ambient surrounded the sample. Increasing of oxygen partial pressure up to 0.2 atm does not affect practically on the linewidth and the linewidth (0.85 mT) is still the same as that in the vacuum conditions. It points out the absence of dipolar/exchange interaction between the localized spins and paramagnetic $O_2$, indicating that absorbed oxygen molecules cannot come close the defect sites in/on the nanodiamond core.

EPR spectra of sample #2 demonstrate that, after prolonged treatment in boiling HCl acid and washing in boiling water, the position, intensity and linewidth of the main ($g\sim 2$) EPR signal remain unchanged ($g=2.0026$, $\Delta H_{\text{pp}}=0.85$ mT at RT; see Fig. 2), but the broad $g\sim 4$ EPR signal practically disappears. It means the main part of ferro- and paramagnetic impurities was removed by HCl treatment and subsequent washing in water. Disappearance of the broad signal reveals two another weak and narrow signals ($g_1=4.26$, $\Delta H_{\text{pp}}=2.9$ mT and

![Fig. 1. The dependence of product $(\chi - \chi_0)\times T$ vs. temperature ($T$) for the hydrochloric acid-purified ND #2. The arrow on the graph indicates the smallest concentration of effective magnetic moments ($S=1/2$) in the system at lowest temperature ($T=1.9$ K), where the AFM short-range ordering takes place. In the inset: so-called Curie–Weiss plot — the dependence of $(\chi - \chi_0)^{-1}$ vs. $T$ for the acid-purified ND #2. This plot is fitted well by a straight line. The data points were collected between 1.9 and 300 K at a magnetic field 0.7 T.](image1)

![Fig. 2. EPR spectra of the main line in purified ND #2 at room temperature (solid line) and $T=4$ K (dashed line).](image2)
$g_2 = 4.00$, $\Delta H_{pp} = 1.4$ mT at $T=4$ K), separated by the distance of 10.4 mT (Fig. 3 lines (a, b)). The effective spin concentration corresponding to these two signals was found to be at least 5 orders of magnitude lower than the same for the main ($g \sim 2$) paramagnetic signal in ND. The origin of this doublet EPR signal, observed in the well purified sample #2, is still under discussion. The dependence of reciprocal integrated intensity vs. temperature demonstrates well-pronounced linear Curie–Weiss behavior at 80 K $\leq T \leq 200$ K, as the same for the main ($g \sim 2$) EPR signal. We supposed that these ($g \sim 4$) signals appear due to so-called “forbidden” $\Delta M = 2$ fine transitions between Zeeman states of thermally populated triplet state of dimers (antiferromagnetically exchange coupled $S=1/2$ paramagnetic defects with $S=1$) sometimes occurring in the ND core: two nearest spins (with the distance between each other of the order of one lattice spacing) may form an isolated exchange coupled dimer. Analysis of relative intensities of main and “forbidden” transition signals evidences that concentration of such dimers may be estimated as just a one isolated dimer per hundred of ND particles.

Low-temperature studies of doublet EPR signal at the half-field region strongly reinforce our hypothesis on non-Fe$^{3+}$-ion origin of that doublet. For the HCl purified sample #2 the EPR spectrum at $g \approx 4$ at room temperature (RT) is a pure doublet with no visible signatures of broad Fe$^{3+}$-ion signal (see Fig. 3 line (a)). However the same sample at 4 K shows superposition of the narrow line doublet and another very weak signal with $g \sim 4.3$, which is narrower than that observed at RT. (see Fig. 3, line (b)). This signal can be ascribed to the remaining of that Fe$^{3+}$-ion signal which could not be observed at RT. At $T=4$ K the line narrowing effect takes place for Fe$^{3+}$-ion signal and this line becomes observable. On the other hand, additionally purified by HyTT sample #3 shows no such a signal at 4 K (see Fig. 3 line (c)). Nevertheless the above mentioned doublet EPR signal remains unchanged. It seems that this observation is a good evidence for justifying that the $g=4$ EPR doublet is an intrinsic feature of the ND sample itself, but not due to extrinsic iron impurities. Appearance of the doublet narrow EPR signals and simultaneous disappearance of broad signal around $g \approx 4.28$ may be considered as a very good practical rule for fabrication of nanodiamonds free from Fe$^{3+}$-ion impurities which are the most common ones even in the well purified ND samples.

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**References**


Fig. 3. EPR spectra of the half-field signals: (a) HCl purified sample #2 at $T=300$ K, (b) the same HCl purified sample #2 at $T=4$ K, (c) additionally purified by hydrothermal treatment sample #3 at $T=4$ K. EPR line parameters found: $g_1 = 4.26 \pm 0.01$, $g_2 = 4.00 \pm 0.01$, $\Delta H_{pp} = 2.9 \pm 0.1$ mT, $\Delta H_{pp} = 1.4 \pm 0.1$ mT, splitting between doublet lines = 10.4 ± 0.1 mT.