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Gadolinium ion bonding on the surface of carboxylated detonation nanodiamond in terms of magnetochemistry and density functional theory

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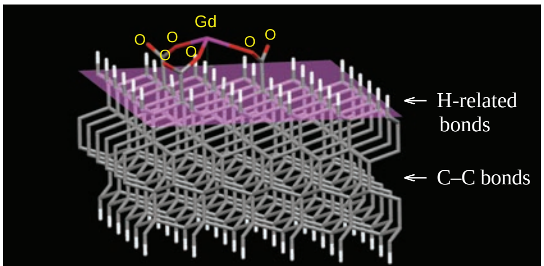
Gadolinium ions (Gd^{3+}) can be fixed on the surface of 5-nm detonation nanodiamonds with terminal carboxyl and/or hydroxyl surface groups. Magnetization curves measured below the temperature of liquid helium at normal pressure give the amount of Gd^{3+} ions of about 18 per a 5-nm nanodiamond particle. The corresponding 2D surface density of ions is smaller than that obtained by density functional theory for a single gadolinium atom fixed on the surface of (111) diamond slab with 36 surface carbon sites with up-standing σ-bonds by a factor of 2.



Wireframe model of Gd^{3+} ion fixation on the (111) surface of covalent diamond lattice

Keywords: detonation nanodiamond, gadolinium ions, surface functional groups, magnetization, low temperatures, density functional theory.

Detonation nanodiamonds (DNDs) with a mean size of about 5 nm are promising for modern chemistry and biochemistry due to their unique ability to bind alien molecular agents and metal cations and carry them in aqueous solutions as nanoplatforms.[1–3] DNDs and their surface-modified derivatives were well described in terms of diamond surface chemistry and the origin of grafted molecules and ligands.[3–6] The surface of as-fabricated DND particles is hydrophilic and covered with oxygen-containing (carboxyl and hydroxyl) functional groups, which give a function to bind third alien agents including metal cations from the environment.[7] DNDs grafted by 3*d* and 4*f* metal ions are promising precursors. Recently, DNDs and other nanosized diamonds grafted by gadolinium ions were synthesized.[8–11] Several articles were devoted to the magnetic and paramagnetic properties of DNDs grafted by Gd^{3+}, but the stereometric and topological details of stable Gd fixation on the DND surface were not investigated.[8,9,11] The fixation of Gd^{3+} ions on the diamond surface was not analyzed theoretically using *ab initio* methods. Previously,[7,12] we identified all oxygen-containing functional groups on the DND surface probed by IR spectroscopy. In contrast to oxygen, nitrogen impurities (to ~2.5 at%) appeared inside the diamond crystallites at the stage of synthesis. They were homogeneously distributed in the diamond cores of fundamental 5-nm DNDs.[13,14] Substitutional nitrogen and interior dangling bonds give the paramagnetic species located inside the crystalline cores of nanodiamond particles.[15]

An independent quantitative characterization of guest metals in such materials together with the determination of their charge status is difficult to perform. Magnetochemistry methods make it possible to precisely characterize the concentration and type of 3*d* and 4*f* metals even the electron spin resonance signals from 4*f*-metal ions are extremely broad, smeared and hardly distinguishable being superimposed with a complicated background and signals from other paramagnetic species. We used these methods for evaluating the maximal surface concentration of Gd^{3+} ions on the DND surface and comparing the data with theoretical predictions for different atomic configurations (only copper-grafted DNDs were studied previously[16,17]).

Here, we reanalyze magnetic characteristics of two powder DND samples: pristine acid-purified and modified with gadolinium as described in detail previously[8,9] and thereafter reproduced (see Online Supplementary Materials, S1). The surface of DND particles in the former was functionalized by oxygen-containing groups (sample ND-ini). The DNDs with the surface saturated with gadolinium to a maximum and dried in a vacuum at 60 °C were labeled as ND-Gd. The nitrogen and surface oxygen contents of ND-ini (the starting material) were ~2.1 and 8.5 at%, respectively, according to X-ray photoelectron spectroscopy (XPS).[†] High oxygen concentration indicates the high degree of filling of DND surface by oxygen-containing groups.

The presence of Gd^{3+} ions on the DND-Gd surface was confirmed by magnetization curves *M(H)* measured at $T = 2$ K with a SQUID magnetometer[‡] (Figure 1, curve *1*). Full magnetization of the DND-Gd sample consists of many contributions including magnetizations related to Curie–Weiss paramagnetism of only interior DND spins and temperature-independent diamagnetism of a diamond lattice (see Online

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[†] A Perkin-Elmer PHI 5600 Multi-Technique XPS system with monochromatized Al Kα radiation was used for this measurement.

[‡] About 20 mg of DND powder sample was disposed in a capsule made of thin aluminium foil, inserted in the middle of a 20-cm quartz tube and sealed after achievement a vacuum (1.2×10^{-5} Torr) inside. Superconducting quantum interference device SQUID MPMS-7 Quantum Design was used.

Supplementary Materials, S2). The plot of magnetization of only alien localized spins (M^{Gd}) *vs.* magnetic field was obtained after the subtraction of the contributions of interior carbon-inherited spins $S_1 = 1/2$ in diamond matrix and linear diamagnetic term ($\chi_o \times H$) related to diamagnetism of cores of carbon atoms from the full magnetization: $M^{Gd}(H) = M(H) - M_{DND}^{S_1=1/2}(H) - \chi_o H$, here $\chi_o = -4.32 \times 10^{-6}$ emu mol^{-1}. The contributions of both terms related to interior carbon-inherited paramagnetism and diamagnetism of diamond matrix itself (Figure 1, curves *3* and *4*) were obtained from a careful analysis of the own magnetization of nondoped pristine DND. The above contributions are exactly the same in pristine and Gd-grafted DNDs. The unique shape of resultant magnetization curve of only alien localized spins (Figure 1, curve *2*) corresponds to the ensemble of localized spins with $S_2 = 7/2$. It was found by applying the Brillouin formula for fitting the experimental magnetization $M^{Gd}(H)$ curve with pronounced saturation trend up to 7 T[18,19] (see S2). Here, S_2 plays the role of *a priory* unknown fitting parameter. The spin value found in the course of fitting (Figure 1, red line) fairly corresponds to the well-known spin of Gd^{3+} ion with seven spin-up 4*f* electrons in electron configuration Xe 4*f*7.[20] The concentration of Gd^{3+} ions ($N_{S_2} \approx 9.5 \times 10^{20}$ ion mol^{-1})[§] was found automatically as a second fitting parameter in the Brillouin formula. It corresponds to the eighteen (and half) spins $S_2 = 7/2$ per one 5-nm particle. The ideal round-shaped 5-nm particle consisting of ~11500 carbon atoms as model DND has only ~1300 (or ~11%) carbon atoms with up-standing σ bonds on the surface. The ratio of the number of bound Gd atoms to the number of such surface sites is 18/1300 ≈ 0.0138.

On the other hand, the concentration of interior spins 1/2 localized inside the DND crystallites is $N_{S_1} \sim 7.57 \times 10^{20}$ spin mol^{-1} or 14–15 spins per a DND particle. This value is approximately the same as the concentration of Gd ions in the system. Note that each of these spin-carrying interior sites in the diamond lattice can be an electron donor or acceptor, which can participate in charge exchange with an alien metal agent or the diamond lattice surface site located just below the metal ion. Meanwhile, we did not find any change in the concentration of interior spins $S_1 = 1/2$ inside DND after the surface grafting by Gd ions,[¶] and all intentionally introduced Gd ions occurred on the surface in the charge state 3+ ($4f^7 5d^0$) having spin $S_2 = 7/2$. We did not also find any contributions from lower spin value paramagnetic spins ($S < 7/2$) among the ensemble of surface alien spins of the DND particles. Thus, Gd^{2+} ions in a low-spin state were absent.

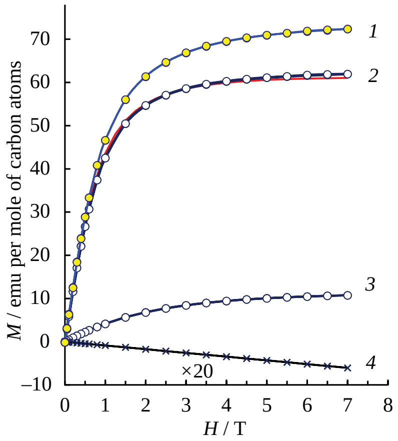

Figure 1 Magnetization curves obtained at $T = 2$ K related to (*1*) full magnetization of DND-Gd sample, (*2*) contribution of only $S_2 = 7/2$ surface Gd^{3+} spins, (*3*) ensemble of interior carbon-inherited own spins of pristine DND particles, and (*4*) diamagnetism of four-coordinated diamond matrix. Curve *2* was obtained after subtraction curves *3* and *4* from the full magnetization of sample. Red line – fitting by means of Brillouin formula for $S_2 = 7/2$ spins. Curve *4* was calculated as $\chi_o H$, where $\chi_o \approx -4.32 \times 10^{-6}$ emu mol^{-1} is an experimental diamagnetic susceptibility of carbon atoms cores C^{4+} (completed shell of eight electrons) found as a fitting parameter. χ_o was extracted from the temperature behavior (χ–T) of magnetic susceptibility of sample following to Curie–Weiss law for both groups of own interior and alien surface spins.

The possible realistic configurations for the fixation of Gd ions on the diamond surface were calculated by a density functional theory (DFT) method for the model of a single Gd atom above the (111) diamond surface of the rhomb-like diamond slab of four layers of carbons consisting of 36 × 8 carbon atoms and passivated from both sides by hydrogen atoms. We used DFT as implemented in the pseudopotential code SIESTA[21] as in our previous studies.[22] The calculations were performed using the generalized gradient approximation (GGA-PBE) with spin polarization[23] and implementation of the correction of van der Waals forces.[24] In the course of optimization, the ion cores were described by norm-conserving nonrelativistic pseudopotentials[25] with cut off radii of 1.14, 1.47, 1.25, 1.20, and 3.09 au for C, O, N, H, and Gd metal, respectively, and the wave functions were expanded with localized orbitals and double-ζ basis set for hydrogen and a double-ζ plus polarization basis set for other atoms. The calculations were carried out with an energy mesh cutoff of 360 Ry and a k-point mesh of 8 × 6 × 4 in the Monkhorst−Pack scheme.[26] The calculated configurations plotted in the Mercury software are shown in Figure 2. In Figures 2(*a*) and 2(*b*), Gd ions are six-coordinated in the dry state and three-coordinated, respectively. In both cases, the Gd^{3+} ions are located ~0.27 nm above the (111) plane of uppermost surface carbon atoms.[††] It is clear that, in the presence of water, the gadolinium ion can be additionally +2 or +3-coordinated by water molecules disposed above. Taking into account that rarer distribution of carboxyl groups over the entire surface of DND particle is more probable, the configuration presented in Figure 2(*b*) is the most realistic, especially, in the case of surface coverage with carboxyl, hydroxyl and anhydride groups and atomic hydrogen. Fixation just by unsaturated dangling σ bond orbital having two electrons with antiparallel spins is shown in Figure 2(*c*). This configuration provides a minimal distance (0.228 nm) between the Gd atom and underlying (111) plane. Additionally, the Gd atom is coordinated by two remaining nitrate[‡‡] groups. The full coordination is 5 in this case, but can be more coordinated (+2, +3) by bonding with water molecules. Comparing the results obtained in this work with published data[16] for water-free copper complexes, we can conclude that Gd ions are fixed almost at the same distances from the diamond surface as the copper ions. Concerning the 2D surface density of Gd ions, we concluded that, from theoretical viewpoint, the piece of (111) diamond surface consisting of 36 carbon atoms can easily bind one Gd ion. The corresponding 2D density or surface atomic ratio is $N_{Gd}/N_C^{surf} = 1/36 \approx 0.0278$ metal ions per surface carbon site. This ratio is two times larger than the corresponding experimental value (0.0138). Such a good agreement suggests that the actual Gd^{3+} content of the diamond surface is probably close to its theoretical limitation. This is because the actual surface of DND particles also contains other kinds of facets like (100) and (110) and terraces that should be also appreciated in bonding if not excluded. Nevertheless, attempts at increasing the Gd content by a factor of at least 2–3 on the DND

[§] The unit ion mol^{-1} means here the number of Gd ions per one mole of carbon atoms.

[¶] We found it by evaluation of the double integrated intensity of main electron paramagnetic signal of DND having a *g*-factor of 2.0027 and no change in its intensity was revealed after functionalization by Gd^{3+}.

[††] These distances are 0.273 and 0.278 nm for panels (*a*) and (*b*), respectively.

[‡‡] Coordinating nitrate groups appear here through their not enough careful removal from obtaining dry material (pellet) fabricated by mixing/agitation of DND suspension in water and water solution of gadolinium nitrate and subsequent pellet extraction.

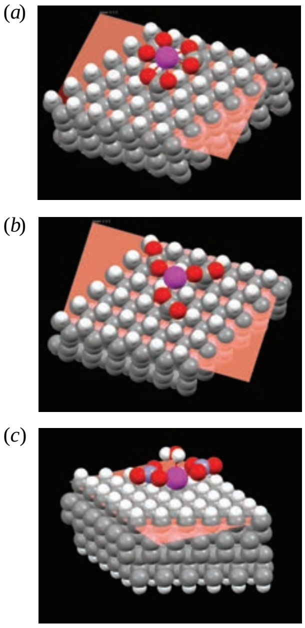

Figure 2 Gd^{3+} fixation on the (111) diamond surface calculated by DFT method for water-free and water-containing complexes incorporating: (*a*) three closely located deprotonated carboxyl groups, (*b*) three distantly located deprotonated carboxyl groups, and (*c*) one surface C* dangling bond, two side nitrate groups and one water molecule. Colors: gray – carbon, white – hydrogen, red – oxygen, blue – nitrogen, violet – gadolinium.

surface are reasonable because the above piece of diamond slab consisting of 36 functionalized surface carbon atoms can bound, in principle, a couple of triply charged metal ions.

According to Figure 2(*c*), Gd-ion complexes on the DND surface can be additionally coordinated by one or two nitrate groups. The Gd^{3+} ions can also be fixed by a pair of neighboring carboxyl groups with an additional coordination by a nitrate group. These nitrate groups are also responsible for the appearance of a sharp δ-like line at 1384 cm^{-1} in the IR spectra[§§] of DND-Gd samples with remaining intentionally undeleted nitrate groups. The analysis[¶¶] of gases appeared in the course of burning of DND-Gd samples having ~18 Gd^{3+} ions per particle in pure oxygen at ~1000 °C showed that the total nitrogen content of these samples was 2.51 ± 0.01 at% *vs.* 2.32 ± 0.015 at% for that of ordinary unfunctionalized DNDs. The excess nitrogen amount of ~0.19 at% should correspond to the nitrogen contain in the remaining surface nitrate groups. The interior nitrogen content of 2.32 wt% corresponds to ~267 nitrogen atoms in the sp^3 crystalline single diamond core. Thus, the above excess amount of surface nitrogen (0.19 at%) corresponds to 22 nitrogen atoms. This value roughly coincides with the amount of Gd^{3+} ions fixed on the DND surface. In the vacuum-treated and dried DND-Gd samples having ~18 Gd^{3+} ions per particle, the nitrogen concentration found by gas analysis (2.13 ± 0.02 at%) was smaller than that in ordinary DND (2.32 ± 0.015 at%). The lack of formally recorded nitrogen in the gas analysis testing (0.19%) of DND-Gd sample is probably related to a smaller amount of released nitrogen gas on the output during the sample burning and gasification rather than a smaller actual nitrogen content in sp^3 diamond cores. This is because metal atoms also serve as nitrogen getters and bound atomic nitrogen from the diamond sp^3 core with the formation of nonvolatile components, which contribute to the ash content.

Thus, the amount of Gd^{3+} ions bound to the surface of nanodiamond particles can be easily evaluated using magnetochemistry methods. The DFT approach confirmed the main schemes for Gd^{3+} fixation on the partially carboxylated diamond surface *via* bonding with three deprotonated carboxyl groups.

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Online Supplementary Materials

Supplementary data associated with this paper can be found in the online version at doi: 10.1016/j.mencom.2020.07.010.

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[§§] The IR absorption spectra were recorded using transparent tablets pressed from a 2 : 1000 mixture of DND powder with KBr of spectroscopic quality (Uvasol®, Merck).

[¶¶] Measurements were performed with Micro Corder JMC10 at an oxygen flow rate of 30 ml min^{-1} in a combustion furnace. Antipyrine was used as a reference substance for calibration.