Paramagnetic Defects and Exchange Coupled Spins in Pristine Ultrananocrystalline Diamonds

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Bulk ultrananocrystalline diamond (UNCD) samples cleaned by acid were investigated by means of electron paramagnetic resonance (EPR) and magnetic susceptibility studies. CW EPR spectra were obtained using commercial X-band EPR spectrometers, (ν = 9 - 9.4 GHz) in the temperature range 4 – 600 K. Two samples were studied: cleaned by only nitric acid (#1) and by nitric acid with the additional treatment by 38% hydrochloric acid (#2).

EPR spectrum of sample #1 consists of two lines: the intensive narrow (ΔH_{pp} = 0.85 mT) line with g = 2.0026, corresponding to the spin concentration of 9-14 spins per particle and the weak broad (ΔH_{pp} ~ 3 mT) one, located in a half-field region (g = 4.26 ± 0.02). The narrow line originates from the existence of dangling C-C bonds located within the surface layers of nanodiamond particle (see ref. [1]). The broad line is directly ascribed to transition metal ions' impurities, mainly rhombically distorted Fe^{3+}-containing complexes located in the vicinity of the nanodiamonds. This fact was well confirmed by magnetic studies at temperature 2 K. Magnetization curve of sample #1 shows significant contribution of spins with S > ? .

EPR spectra of sample #2 demonstrate that, as a result of prolonged treatment in boiling HCl acid and washing in boiling water, the broad g ~ 4 EPR signal practically disappears. It indicates the main part of ferro- and paramagnetic impurities was removed by HCl treatment and further washing in water. Disappearance of the broad signal reveals two another weak narrow and signals (g_1 = 4.25, ΔH_{pp} = 2.9 mT and g_2 = 3.99, ΔH_{pp} = 1.1 mT at T = 5 K), separated by the distance of 10.5 mT. The effective spin concentration, corresponded to these two signals, was found to be 5 orders of magnitude lower then the same for the main (g ~2) paramagnetic signal in UNCD. The origin of this doublet EPR signal, still observed in the well purified sample, is discussed. The dependence of reciprocal integrated intensity vs. temperature demonstrates well-pronounced linear Curie-Weiss behavior at 80 K ≤ T ≤ 200 K, as the same for the main (g ~ 2) EPR signal. We supposed that these (g ~ 4) signals appear due to "forbidden" ΔM = 2 fine transitions between Zeeman states of thermally populated triplet state of dimers (antiferromagnetically exchange coupled S = ? paramagnetic defects with S = 1) sometimes occurring in the UNCD core: two nearest uncoupled spins (with the distance between each other of the order of one lattice spacing) may form an isolated dimer. Analysis of relative intensities of main and "forbidden" transition signals evidences that concentration of such dimers amounts just isolated dimers per thousand of UNCD particle. Consequent study of magnetic properties on the same samples, done using SQUID magnetometer, showed that magnetic phenomena in nanodiamonds are caused by localized spins with S = ? ., most part of them are weakly antiferromagnetically coupled that the deviation from Curie law takes place at temperatures below 20 K.

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