MAGNETIC PROPERTIES OF THE NATURAL AND ISOTOPE-MODIFIED DIAMOND AND SILICON CARBIDE

Taldenkov A.N. [1,*], *Inyushkin A.V.*[1], *Chistotina E.A.*[1], *Ralchenko V.G.*[2], *Bolshakov A.P.*[2], *Mokhov E.N.*[3]

[1]NRC "Kurchatov Institute", Moscow, 123182, Russia
[2]A.M. Prokhorov General Physics Institute RAS, Moscow, Russia
[3]Ioffe Physico-Technical Institute RAS, St. Petersburg, Russia

Abstract. The magnetic properties of single crystals of synthetic diamond and crystals of silicon carbide were studied. High-purity samples of diamonds synthesized with HPHT and CVD technologies were used. The crystals of silicon carbide were grown by sublimation and industrial technology. Along with samples with a natural isotopic composition, monoisotopic crystals of diamond (99.96% ^{12}C and 99.96% ^{13}C) and silicon carbide (99.993% of ^{28}Si) were studied. On the basis of the data obtained, the diamagnetic susceptibility was determined and the concentration of paramagnetic centers and the content of the ferromagnetic component were evaluated. The results are discussed.

1 Introduction

One of the trends in solid-state electronics is the increasing research activity in the field of wide-gap semiconductors – silicon carbide and diamond. The transport of spin-polarized electrons attracts special attention of theorists and experimenters.

The main channel for the relaxation of the electron spin is the scattering on nuclear magnetic moments of the odd isotopes of carbon ^{13}C and silicon ^{29}Si. For this reason, the investigation of isotopically modified crystals is an urgent task.

Diamond is regarded as an ideal material for spin transport and promising "quantum computations". Due to the weak orbital interaction in comparison with other materials, a very long spin diffusion length is expected in it. In isotopically pure diamond, where the content of ^{13}C isotope is reduced, the spin relaxation time may exceed 1 ms at room temperature. Despite the great progress in the production of synthetic diamonds, their magnetic properties remain practically unstudied. Nothing like a study of the magnetic properties of natural diamonds [1] was made for synthetic diamonds. Magnetic properties of synthetic diamonds with modified isotopic composition have been also not studied yet.

Investigation of the magnetic properties of SiC became very important after the detection of ferromagnetism (FM) in SiC crystals [2]. FM was induced by neutron irradiation, neon and xenon ions, protons, and also by doping with aluminium. The combination of ferromagnetism and isotopic modification in one crystal can be promising for the creation of effective spin transport.

2 Experimental details

The magnetic moments of the crystals were measured with MPMS XL-7 SQUID magnetometer (Quantum Design) using the reciprocating sample option (RSO) in temperature range temperature 2 K < T < 300 K and in magnetic field H < 7 T.

SiC single crystals under investigation were produced with various techniques (Table 1). Samples #2 is the crystal ^{28}SiC with 99.993% of ^{28}Si and sample #1 is its counterpart with natural isotopic abundance. Both were synthesized with low temperature sublimation technique. Sample #3 was grown with high temperature Lely technique. Samples #4 – #13 were synthesized with industrial technique: #5 and #6 are 6H and 4H substrates made by CREE Inc. ($n = 10^{18}$ cm^{-3}); 6H crystals #8 and #9 were irradiated with neutron dose about 2.2×10^{18} and crystal #7 is its unirradiated counterpart; samples #10 and #11 are 6H crystals with free carrier concentration of $n \sim 10^{16}$ cm^{-3} and $n \sim 10^{18}$ cm^{-3}; samples #12 and #13 are 6H SiC crystals doped with Fe.

The samples of synthetic diamond have been grown by high-pressure high-temperature process (HPHT) #1 and CVD method (samples #3 - #7) (Table 2). High-purity CVD single crystals, #3 from Element Six Corp., #1 from New Diamond Technology (Russia), and #4 synthesised in General Physics Institute, RAS (Moscow), were investigated. Also, the unique diamond crystals #5 with isotope ^{13}C concentration 99.96% and #6 enriched with ^{12}C to 99.96% obtained by the CVD method also were studied. The CVD diamond #7 had unique light pink colour. The pure natural diamond #2 was investigated for comparison.

* Corresponding author: box-n3@bk.ru

3 Results and discussion

The characteristic magnetization dependencies measured at permanent temperature are shown in Fig. 1a. Three main contributions can easily be distinguished: diamagnetic, paramagnetic, and ferromagnetic. The diamagnetic term can be seen as linear in field

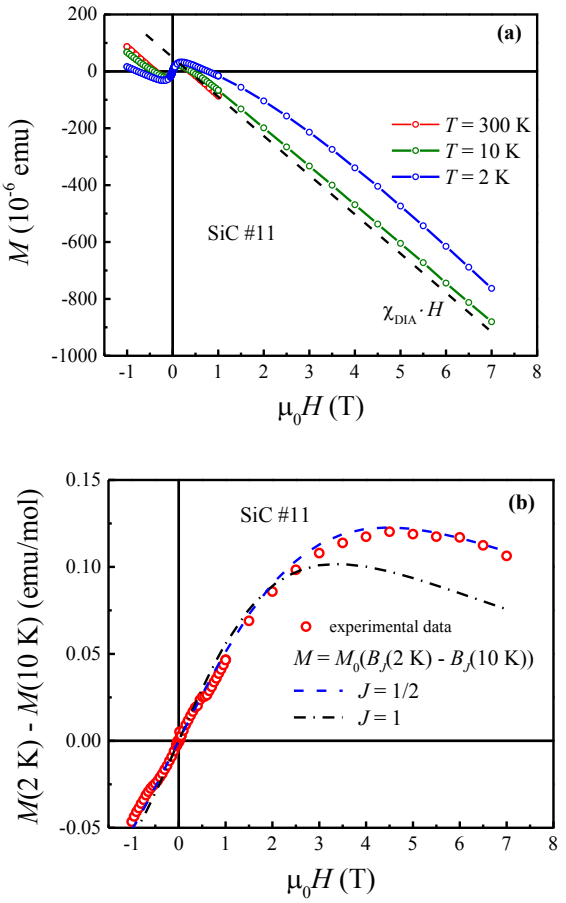

Fig. 1. The isothermal magnetization curves at different temperatures (a), dash line demonstrates diamagnetic contribution at T = 300. The field dependence of difference $\Delta M(H) = M(2\text{ K}) - M(10\text{ K})$ (b). Lines were computed with difference of the Brillouin functions $M_0 B_J(x)$ with saturation value M_0.

contribution $\chi_{DIA2} \cdot H$ at high temperature. The FM contribution with saturated value M_{FM} is manifested in the form of singularities at $H < 1$ T in the entire temperature range. The paramagnetic contribution can be identified by saturation in high fields at the lowest temperature. It can be assumed that terms $\chi_{DIA2} \cdot H$ and M_{FM} do not depend on temperature at $T < 20$ K. The field dependence of the difference $\Delta M(T_1,T_2) = M(T_1,H) - M(T_2,H)$ contains only the paramagnetic contribution, and can be described using Brillouin function $B_J(x)$, where $x = gJ\mu_B B/k_B T$. In this case, the quantum number J and the concentration of the paramagnetic centres N_{P2} are free fitting parameters. An example of such data treatment is shown in Fig. 2b. For most crystals, the value of J was close to 1/2 and never exceeded unity.

The temperature dependencies of molar static susceptibility $\chi_M = (M(T,H) - M_{FM})/H$ in applied field $\mu_0 H = 1$ T are shown on Fig. 2. Susceptibility was fitted with Curie-Weiss function $\chi_M(T) = \chi_{DIA1} + C/(T - \Theta)$, with χ_{DIA1}, C and Θ as the free parameters. The value of Θ was less than 2 K. Using the Curie-Weiss constant C one can estimate the concentration of paramagnetic

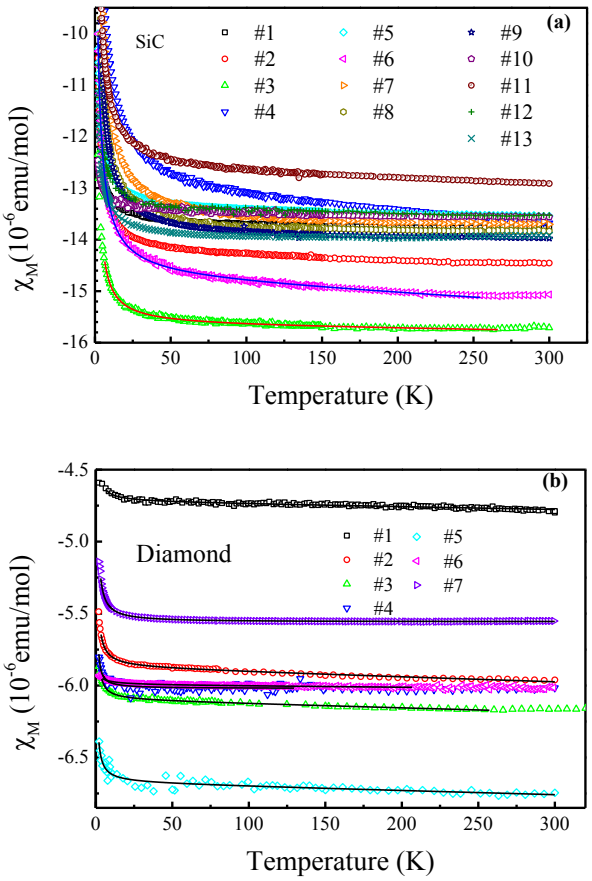

Fig. 2. Temperature dependencies of the static susceptibility of silicon carbide (a) and diamond (b). Lines are approximation by the Curie-Weiss law.

centers N_{P1} with spin J. The results of the processing of all the data are presented in Tables 1 and 2.

The diamagnetic susceptibility χ_{DIA} is about -13.5 emu/mol for most of the crystals within 10% range. It is close to the value published in Ref. [2] for unirradited 6H SiC sample synthesised by industrial technique. Significant change in χ_{DIA}, exceeding the experimental error, is observed for crystal #3. This sample was grown by the high-temperature method, and it can be assumed that it has the lowest concentration of vacancies.

There is a positive correlation between the measured values of paramagnetic centers N_P and the free carrier concentrations (#10 and #11). Thus, the measurement of low-temperature paramagnetic contribution to the static magnetization demonstrates the possibility to determine the concentration of electrically active impurities. The

Table 1. Parameters of the single crystals of SiC

#	$-\chi_{DIA1}$ (emu/mol)	$-\chi_{DIA2}$ (emu/mol)	M_{FM} (emu/g)	N_{P1} (cm^{-3})	N_{P2} (cm^{-3})
1	$12.8\cdot10^{-6}$	$13.7\cdot10^{-6}$	$2.0\cdot10^{-4}$	$7.9\cdot10^{17}$	$7\cdot10^{17}$
2	$14.3\cdot10^{-6}$	$14.3\cdot10^{-6}$	$6.8\cdot10^{-4}$	$1.2\cdot10^{18}$	$1.0\cdot10^{18}$
3	$15.5\cdot10^{-6}$	$15.9\cdot10^{-6}$	$3.3\cdot10^{-4}$	$1.1\cdot10^{18}$	$9\cdot10^{17}$
4	$12.9\cdot10^{-6}$	$13.2\cdot10^{-6}$	$2.13\cdot10^{-3}$	$1.5\cdot10^{18}$	$7\cdot10^{17}$
5	$13.4\cdot10^{-6}$	$13.4\cdot10^{-6}$	$3.9\cdot10^{-4}$	$1.1\cdot10^{18}$	$1.0\cdot10^{18}$
6	$15.0\cdot10^{-6}$	$14.8\cdot10^{-6}$	$5\cdot10^{-5}$	$2.0\cdot10^{18}$	$1.3\cdot10^{18}$
7	$13.7\cdot10^{-6}$	$13.8\cdot10^{-6}$	$4\cdot10^{-5}$	$3.2\cdot10^{18}$	$2.5\cdot10^{18}$
8	$13.8\cdot10^{-6}$	$14.0\cdot10^{-6}$	$1.2\cdot10^{-4}$	$2.6\cdot10^{18}$	$1.6\cdot10^{18}$
9	$13.8\cdot10^{-6}$	$14.0\cdot10^{-6}$	$3.3\cdot10^{-4}$	$2.4\cdot10^{18}$	$1.9\cdot10^{18}$
10	$13.6\cdot10^{-6}$	$13.4\cdot10^{-6}$	$4\cdot10^{-5}$	$1.3\cdot10^{17}$	$1.2\cdot10^{17}$
11	$12.9\cdot10^{-6}$	$12.7\cdot10^{-6}$	$1.26\cdot10^{-3}$	$2.0\cdot10^{18}$	$3.5\cdot10^{18}$
12	$13.8\cdot10^{-6}$	$13.9\cdot10^{-6}$	$2.1\cdot10^{-4}$	$1.0\cdot10^{18}$	$1.5\cdot10^{18}$
13	$13.5\cdot10^{-6}$	$13.5\cdot10^{-6}$	$2\cdot10^{-5}$	$7\cdot10^{17}$	$7\cdot10^{17}$

χ_{DIA1} is calculated from $\chi(T)$. χ_{DIA2} is calculated from $M(H)$ at $T > 150$ K. M_{FM} is the ferromagnetic contribution evaluated from $M(H)$ at $T > 150$ K. N_{P1} is the concentration of the paramagnetic centers evaluated from the Curie-Weiss law at $2\text{ K} < T < 300\text{ K}$. N_{P2} is the concentration of paramagnetic centers evaluated from the fitting of the $M(H)$ at $T = 2$ K with Brillouin functions. One mole of natural SiC is 40.0962 g.

SiC crystal #2 enriched with ^{28}Si has a concentration of paramagnetic impurities close to that observed in the crystal #1 with the natural isotopic composition. In general, crystals obtained by the low-temperature sublimation technique in their parameters are not inferior to crystals grown by industrial high-temperature method.

Single crystals #8 and #9 of silicon carbide irradiated with a neutron flux have an increased concentration of the ferromagnetic component compared to the pristine crystal #7. The rest parameters of these samples are similar. It can be assumed that the main result of irradiation is the formation of $V_{Si}V_C$ divacancies, as suggested in [2]. The maximal value of M_{FM} is nearly the same as that published in [2] for irradiated crystals. For the samples #12 and #13 doped with iron, we have not observed any significant effect of the doping on their magnetic properties.

For diamonds the diamagnetic susceptibility χ_{DIA} of four of our single crystals is about $-6\cdot10^{-6}$emu/mol. Magnetic susceptibility in natural diamonds ranging from $-5.5\cdot10^{-6}$emu/mol to $-4.9\cdot10^{-6}$ emu/mol was obtained in Ref. [1] and values $-5.9\cdot10^{-6}$emu/mol and $-5.4\cdot10^{-6}$emu/mol was published in Refs. [3] and [4] correspondingly. Despite the fact that our data are systematically lower, these results are considered to be relevant to each other. The values of χ_{DIA} observed in crystals #1 and #5 are considerably knocked out from the range under consideration. We cannot follow assumption in Ref. [1] that the larger value of χ_{DIA} in sample #1 is due to the significant content of the FM phase, since measured M_{FM} was not large, and was subtracted when determining χ_{DIA}. Perhaps this result relates to the

Table 2. Parameters of the single crystals of diamonds

#	$-\chi_{DIA1}$ (emu/mol)	$-\chi_{DIA2}$ (emu/mol)	M_{FM} (emu/g)	N_{P1} (cm^{-3})	N_{P2} (cm^{-3})
1	$4.7\cdot10^{-6}$	$4.8\cdot10^{-6}$	$2.6\cdot10^{-5}$	$2.7\cdot10^{17}$	$1.6\cdot10^{17}$
2	$5.7\cdot10^{-6}$	$5.9\cdot10^{-6}$	$3.2\cdot10^{-4}$	$4.1\cdot10^{17}$	$3.1\cdot10^{17}$
3	$6.1\cdot10^{-6}$	$6.1\cdot10^{-6}$	$5.0\cdot10^{-4}$	$2.6\cdot10^{17}$	$2.2\cdot10^{17}$
4	$6.0\cdot10^{-6}$	$6.0\cdot10^{-6}$	$8.0\cdot10^{-5}$	$1.8\cdot10^{17}$	$2.2\cdot10^{17}$
5	$6.7\cdot10^{-6}$	$6.7\cdot10^{-6}$	$6.3\cdot10^{-5}$	$3.2\cdot10^{17}$	$1.3\cdot10^{17}$
6	$6.0\cdot10^{-6}$	$6.0\cdot10^{-6}$	$7.2\cdot10^{-5}$	$9\cdot10^{16}$	$4\cdot10^{16}$
7	$5.5\cdot10^{-6}$	$5.6\cdot10^{-6}$	$<5\cdot10^{-6}$	$4.6\cdot10^{17}$	$4.3\cdot10^{17}$

Notations are the same as in **Table** 1. One mole of natural diamond is 12.01 g.

processes occurring during HPHT synthesis. A significantly lower value for sample #5 may be caused by isotope effect due to large change in atomic mass in ^{13}C diamond. But we have to note, that a systematic error for sample #5 may by enhanced due to small sample mass (6.32 mg).

The isotopically engineered crystals have concentration of paramagnetic impurities and ferromagnetic inclusions close to that in crystal commercially available in the market. The parameters of crystal ^{12}C(99.96%) #6 slightly differ from the parameters of crystal #4, which can be considered as a counterpart with a natural isotopic content. Moreover, the paramagnetic contribution received in isotopically pure crystal #6 is the lowest among all measured samples, which indicates its chemical purity. The paramagnetic contribution estimated in CVD and HPHT crystals are generally close to each other and the best samples of synthetic diamonds are superior in quality to natural.

The work is supported by RFBR grants 16-07-00979 and 16-0701188, and by the RSF grants 16-42-01098 and 14-12-01403.

References

1. A. Sigamony, Indian Acad. of Science, Proc.A, **19** (1944), p.310-314.
2. Yutian Wang et al., Scientific Reports **5** (2015), 8999.
3. S. Hudgens, M. Kastner, and H. Fritzsche, Phys. Rev. Lett. **33** (1974), 1552.
4. J. Heremans, C.H. Olk, and D.T. Morelli, Phys. Rev. **49** (1994), 15122.