Abstract. Polarized negative muons were used to study the behaviour of the boron acceptor centre in diamond produced by the chemical vapour deposition (CVD) method. The temperature dependence of the muon spin relaxation rate and spin precession frequency were measured in the range of 20 – 330 K in a transverse magnetic field of 14 kOe. The muon polarization amplitude \( P(t = 0) \) does not depend on the temperature and the muon spin relaxation rate decreases as the temperature increases. For the first time a negative shift of the muon spin precession was observed in diamond. The measurements show that the magnetic susceptibility of the CVD sample is negligible (\( \chi = -4.13(2) \cdot 10^{-7} \text{cm}^3/\text{g} \) at 20 K) and it could not be the reason of the negative shift muon spin precession frequency. The negative shift of the muon spin precession frequency is tentatively attributed to an anisotropic hyperfine interaction in the boron acceptor in diamond.

Diamond with its unsurpassed mechanical strength, thermal conductivity, and radiation hardness is a promising semiconductor for particle detectors and electronic components capable of withstanding high heat and radiation loads. Great advances have been made over the last years in the technology of manufacturing synthetic single crystal diamond and diamond films [1, 2].

Boron is the only dopant which forms an acceptor centre (AC) in diamond with an ionization energy of \( \approx 370 \text{ meV} \) [3]. The metal-insulator transition occurs at a concentration of \( \approx 2 \cdot 10^{20} \text{ cm}^{-3} \) of boron atoms [4]. The EPR signal of boron impurities in diamond was observed only for uniaxially stressed samples [5], and the electronic state of this acceptor is investigated insufficiently.

The possibility of using negative muons to study the behaviour of acceptor impurities in diamond arises from the fact that capture of a negative muon by a carbon atom results in the formation of a muonic atom \( \mu_B \) with an electron shell that is analogous to that of the boron atom. The evolution of the polarization of \( \mu^- \) in the 1s atomic state depends on the interaction of the muon spin with the electron shell of the muonic atom and on the interactions of this muonic atom as AC with the crystal lattice. Providing that the electron shell of \( \mu_B \) has a nonzero magnetic moment (paramagnetic \( \mu_B \)), there is a hyperfine interaction between the muon and the electron shell. The efficiency of the hyperfine interaction depends on the relaxation rate \( \nu \) of the magnetic moment of \( \mu_B \) and on the hyperfine interaction constant \( A_{hf} \). According to theoretical calculations [6], relaxation of the muon spin and a paramagnetic shift of its precession frequency are expected for \( \nu \gg |A_{hf}| \). Under the assumption of an isotropic hyperfine interaction, the
paramagnetic shift should be of positive sign and inversely proportional to temperature.

The boron atom as AC in diamond may be in the diamagnetic (B\textsuperscript{−}) or paramagnetic (B\textsuperscript{−} + \hbar) state. In the latter case a hole is localized in vicinity of the AC. At equilibrium the boron acceptor in diamond is expected to be paramagnetic below \( \approx 300 \) K. In earlier experiments \cite{7} we observed no frequency shift of the muon spin precession in diamond at the level of \( 5 \cdot 10^{-3} \). The goal of the present experiment was to improve the accuracy of the muon spin precession frequency measurement.

1. Diamond sample and measurements

The diamond sample was produced on Si substrates by a microwave plasma assisted chemical vapour deposition (CVD) technique in the CH\textsubscript{4}/H\textsubscript{2} mixtures at the Institute of General Physics of RAS (Moscow, Russia) \cite{9}. The typical growth conditions were as follows: 1.2 or 2.0\% methane concentration in the mixture, total gas flow rate 1000 sccm, pressure 90 or 100 Torr, the substrate temperature of 720\°C or 820\°C. While the grain size on substrate side was about 1 \( \mu \)m, the crystallites of up to 200 \( \mu \)m were revealed on the opposite growth side of the films. It was found from the infrared and ultraviolet optical absorption measurements that the main impurities in the sample were hydrogen (\( \approx 70 \) ppm) and substitutional (paramagnetic) nitrogen atoms (\( \approx 1.5 \) ppm) \cite{10}). In CVD diamond nitrogen is contained predominantly in the substitutional form. Other impurities were less than 0.1 ppm. The hydrogen atoms (CH bonds) are located mostly on grain boundaries \cite{11}. After chemical etching of the substrate the cylinder-shaped sample D6 with the diameter 25 mm and height 1.3 mm (thickness 0.427 g/cm\textsuperscript{2}) for the µSR study, and two bricks (samples A and B) with the dimensions 3x1.5x1.5 mm\textsuperscript{3} (weight 34 mg) for magnetic measurements were cut using a laser. The DC magnetization measurements of the samples A and B were performed with the Quantum Design SQUID magnetometer.

The µSR experiment was performed with the upgraded ALC instrument \cite{8} located at the πE3 muon beam line of the proton accelerator of the Paul Scherrer Institute in Switzerland. In the πE3 beam line the muons were ”transversely” polarized – the angle between the muon spin and the muon momentum was \( \sim 45^\circ \). The polarization of negative muons in synthetic diamond was studied in the magnetic field of 14 kOe in the temperature range of \( 20−330 \) K. One additional measurement was performed in 3.0 kOe at 140 K. The magnetic field at the sample was parallel to the momentum of the incoming muon. The time-differential µSR spectrum was measured with a CAEN V1190B time-to-digital converter (TDC), bin width was 0.39 ns and the total number of bins in the spectrum was 26000. About 85\% of the incoming muons stopped in the sample and 15\% in the copper holder. As a reference, a graphite sample (diameter 26 mm and thickness 0.66 g/cm\textsuperscript{2}) was measured by µSR under the same conditions as the diamond sample.

The time distribution of electrons from the \( \mu^- \rightarrow e^- \) decay was fitted by the function

\[
N(t) = N_0(C)[1 + A(t)\text{e}^{-t/\tau(C)}] + N_0(Cu) \cdot \text{e}^{-t/\tau(Cu)} + bg
\]

\[
A(t) = a \cdot P(t) = a \cdot F_0 \cdot \text{e}^{-R \cdot t} \cdot \cos(\omega t + \varphi)
\]

where \( N_0(C) \) (\( N_0(Cu) \)) is proportional to the number of muons stopped in the sample (in the copper holder); \( \tau(C) \) (\( \tau(Cu) \)) is the mean lifetime of the muon in the 1s state of carbon (copper); \( a \) is the coefficient of asymmetry of the space distribution of electrons taking into account the actual parameters of the spectrometer; \( F_0 \) is the muon polarization in the 1s state at \( t = 0 \); \( R \) is the muon spin polarization damping rate; \( \omega \) and \( \varphi \) are the frequency and the initial phase of the muon spin precession in the magnetic field, and \( bg \) is the time-independent background.

The muon polarization \( F_0 \) in the 1s state of copper is close to zero due to the hyperfine interaction of the muon spin with the spin of the nucleus and due to very fast transitions between the levels \( F_+ = I + S_\mu \) and \( F_− = I − S_\mu \), where \( I \) is the spin of the copper nucleus and \( S_\mu \) is the muon spin (see \cite{12, 13, 14}).
Figure 1. The $\mu^-$SR spectrum for the diamond sample D6 at 27 K after background subtraction and correction for the negative muon lifetime. The line corresponds to fitting the data with function (1).

An example of the fragment of $\mu^-$SR spectrum measured for the diamond sample at 27 K in the magnetic field of 14 kOe is presented in Fig 1.

2. Results and discussion
The behaviour of the muon spin polarization in the reference graphite sample was studied at temperatures 9.6, 50, 100, 200, and 300 K in a magnetic field of 14 kOe. It was observed that in graphite the muon spin polarization and the frequency of the muon spin precession do not depend on temperature: $[P_0(T) - P_0(300 \text{ K})]/P_0(300 \text{ K}) \lesssim 0.06 \pm 0.08$ and $\Delta \omega/\omega = [\omega(T) - \omega(300 \text{ K})]/\omega(300 \text{ K}) \lesssim (6 \pm 4) \cdot 10^{-5}$ (see also [14]). The relaxation of the muon spin in graphite was not observed within the accuracy of the measurements ($R < 0.05$ MHz).

The results of the measurements on the CVD diamond are shown in Fig. 2. The muon polarization damping rate depends on temperature as $R \sim 1/T^{0.8}$ in the range of 20 – 80 K (solid line in Fig. 2) and as $R \sim 1/T^{2.0}$ in the range of 80 – 230 K (dotted line). A strong drop of the damping rate at $\sim 250$ K and no damping at 300 and 330 K were observed. There is no difference in the damping rate of the muon spin at 140 K in the magnetic field of 3.0 kOe compared to 14 kOe. Generally, the temperature dependence of $R$ in sample D6 is similar to that observed earlier for the CVD film samples in 1.5 and 2.5 kOe magnetic fields [7].

In the sample D6 the muon polarization amplitude $P_0$ does not depend on temperature and it is approximately 16 % larger than in the reference carbon sample.

As seen in Fig. 2, the muon spin precession frequency in the carbon reference sample does not depend on temperature. At room temperature ($T = 300$ K) the muon spin precession frequency in the D6 sample is close to that in the reference sample: $[\omega(C) - \omega(D6)]/\omega(C) = (1.8 \pm 0.4) \cdot 10^{-4}$. Opposite to the theoretical prediction [6] and to the experimental results in silicon [15], a negative shift of the muon spin precession frequency was observed at temperatures below 250 K. The temperature dependence of the frequency shift can be approximated as
Figure 2. Damping rate $R$ and precession frequency shift $\Delta \omega / \omega$ of the negative muon spin measured in the synthetic CVD diamond sample D6 in the magnetic field of 14 kOe.

$[\omega(T) - \omega(300 \text{ K})] / \omega(300 \text{ K}) = \Delta \omega / \omega \sim -1/T$ (dotted line in Fig. 2).

The negative shift of the muon spin precession frequency may be due to three different reasons: a) it may be due to the presence of other paramagnetic defects (excluding the acceptor centres) in diamond. The magnetic field at the muon could differ from the external field because of polarization of these paramagnetic defects. For example, $N_0$ and $H1(H2)$ paramagnetic centres were observed in polycrystalline CVD diamond by EPR [10];

b) let us assume that the muonic atom is formed in the $\mu B^0$ state within a time less than $10^{-9}$ s and that the transition rate from this state to the equilibrium one ($\mu B^- + h$) is smaller than the muon decay rate. In the state $\mu B^0$ the muonic atom has covalent chemical bonds with three nearest carbon atoms, and the fourth carbon atom has an electron with an unpaired spin (one dangling bond). The polarization of this paramagnetic complex in an external magnetic field could result in the negative shift of the muon spin precession frequency;

c) negative frequency shift can also be due to polarization of the paramagnetic acceptor centre in the magnetic field if the muonic atom is formed in the ($\mu B^- + h$) state in $\approx 10^{-8}$ s and the hyperfine interaction in the AC is anisotropic. In the state ($\mu B^- + h$) the muonic atom has covalent chemical bonds with all four nearest carbon atoms and a hole localized in the vicinity of AC.

The frequency shift of the muon spin precession should be proportional to the susceptibility of the paramagnetic defects or to the susceptibility of the paramagnetic acceptor centres if $\nu \gg |A_{hf}|$. Therefore, a simple $1/T$ (Curie type) temperature dependence of the muon spin precession frequency shift is expected.

To elucidate the effect of paramagnetic (magnetic) defects on the muon spin precession frequency we measured the magnetic susceptibility of our sample. The magnetic moments ($M$) of samples A and B were measured in magnetic fields in the range of 0–50 kOe at the temperatures 20, 100, and 300 K. The temperature dependence $M(T)$ was studied in detail in the magnetic fields of 95.2 Oe and 20.0 kOe for both samples. The results for both samples A and B are similar within the accuracy of the measurements. The results of the measurements for sample A are presented in Fig. 3 and in Fig. 4. There is evident linear dependence of the magnetic moment on the magnetic field in the range from 0 to 50.0 kOe. The susceptibility of the sample was $\chi = -4.13(2) \cdot 10^{-7}$ cm$^3$/g, $-4.29(2) \cdot 10^{-7}$ cm$^3$/g, and $-4.36(2) \cdot 10^{-7}$ cm$^3$/g, at the temperatures 20, 100, and 300 K, respectively. The value of $\chi$ for the synthetic CVD sample is in agreement with that for natural diamond [16, 17]. As seen from Fig. 4, the magnetic moment of the sample in the 95.2 Oe and 20.0 kOe magnetic field practically does not depend on temperature in the range of 20 – 300 K. Only at temperatures below 20 K the magnetic moment slightly increases.
**Figure 3.** Magnetic moment of CVD diamond sample A vs the magnetic field: ⋄ at 20 K and ● at 300 K.

**Figure 4.** Temperature dependence of the magnetic moment of the synthetic CVD diamond: ⋄ in the magnetic field of 95.2 Oe and ● in 20.0 kOe. For better visualization in one single graph the value of $M$ at the magnetic field of 20.0 kOe was scaled by 1/210

with decreasing temperature. Therefore, the concentration of magnetic impurities (defects) in our CVD sample is negligible and cannot produce the observed frequency shift. Moreover, the muon spin precession frequency shift depends on temperature as $\sim -1/T$ in the range of 20 − 300 K, where the magnetic moment of the sample is practically constant.

The measured values of $P_0$ at different $T$ are close to the maximum possible muon polarization in the 1s state of a carbon atom. This means that the muonic atom $\mu$B is formed in one of the chemically bonded $\mu$B$^0$ or $(\mu B^1 + h)$ states with a probability close to unity in less than 10$^{-9}$ s. It is worth mentioning that the Auger transitions of the muon destroy chemical bonds of the muonic atom with neighbouring carbon atoms. Theoretical calculations [18, 19] suggest that the muonic atom in diamond restores chemical bonds and is formed in the $\mu$B$^0$ state within 10$^{-10} − 10^{-9}$ s.

At present we do not have an analytical expression for the relaxation of the muon spin if there
is an anisotropic hyperfine interaction in the muonic atom. Nevertheless, we may assume that $R$ is inversely proportional to the relaxation rate of the magnetic moment of the acceptor centre in both $\mu B^0$ and $(\mu B^{1-} + h)$ states. In diamond relaxation of the magnetic moments of $\mu B^0$ and $(\mu B^- + h)$ should be attributed to scattering of phonons by these centres. Direct, Raman, and Orbach processes can contribute to phonon scattering, and the temperature dependence of the probability of these processes is very different [20]. In the present experiment two temperature domains with different temperature dependences of the relaxation rate of the muon spin were observed. Thus, we conclude that there is a contribution of two different processes to scattering of phonons at the acceptor in diamond. The dominance of one process over the other reverses at about 80 K. According to the calculations for the acceptor in silicon, the Raman process overcomes the direct (one phonon) process at $T = 8$ K, and the Orbach process is negligible below 100 K [20].

3. Conclusion
A large negative shift of the precession frequency of the negative muon spin in diamond was found for the first time. Simple Curie type $\Delta \omega/\omega \sim -1/T$ temperature dependence of the frequency shift was observed. It is not excluded that the muonic atom as an AC forms in the equilibrium $(\mu B^- + h)$ state in $10^{-8}$ s and there is an anisotropic hyperfine interaction in AC. The temperature dependence of the relaxation rate of the muon spin evidences that two different processes contribute to phonon scattering by the acceptor centre in the temperature range of $20 - 250$ K.

The magnetic measurements showed that the magnetic susceptibility of the CVD sample was close to that of the purest natural diamond.

The authors are grateful to prof. Yu. M. Belousov for fruitful discussions. We thank the Directorate of the Paul Scherrer Institute for giving us the possibility of carrying out the experiments at PSI.

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