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Magnetoresistance and magnetic susceptibility of doped Si–Ge whiskers

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The magnetoresistance and magnetic susceptibility (MS) of Si–Ge<B> whiskers have been determined in the temperature range 4.2–300 K in magnetic fields up to 140 and 4.0 kOe, respectively. The results obtained show two peculiarities: a substantial paramagnetic contribution to the whisker MS and magnetization, non-linear dependency of magnetization on magnetic field. These facts indicate the existence of antiferromagnetic ordering in the whiskers. The magnetization hysteresis really observed at 4.2 K confirms the above supposition. Possible reasons of the effect revealed are discussed.

Определены магнетосопротивление и магнитная восприимчивость (МВ) нитевидных кристаллов (НК) Si–Ge<B> в диапазоне температур 4,2–300 К в магнитных полях соответственно до 140 кЭ и 4,0 кЭ. Полученные результаты имеют две особенности: парамагнитный вклад в МВ и намагниченность и нелинейная зависимость намагниченности от магнитного поля. Эти факты говорят о присутствии антиферромагнитного упорядочения в НК. Наблюдение гистерезиса намагниченности при 4,2 К подтверждает это предположение. Обсуждаются возможные причины обнаруженного эффекта.

Si–Ge solid solution whiskers are used as sensors of various physical parameters (temperature, pressure, strain) operating in wide range of temperatures including cryogenic ones [1]. Investigation of magnetic properties of the whiskers is an actual task both from practical and fundamental point of view. On the one hand, the whisker magnetic response determines a possibility of sensor application under magnetic fields. On the other hand, investigation of magnetic susceptibility (MS) allows to improve knowledge about magnetoresistance and conduction of the crystals, their behavior under various external influences, the interaction nature of the effects, etc. Finally, the whiskers are of interest due to numerous size effects. Among those, there is a decrease of lattice parameter [2], a shift of energy bands, luminescence in visible range arising at decrease of the whisker diameter down to less than 1 μm [3], size dependence of magnetic susceptibility Si whiskers which differs from that of bulk material [4]. It is worth to note that magnetization studies of bulk p–Si were carried out in numerous works, in particular, in [5–7]. Authors [5] provided the results of magnetic investigations of bulk Si doped with B in wide ranges of impurity concentration, temperature and magnetic field strength. In particular, it was shown that magnetic susceptibility of heavily doped Si samples has negative sign and depends hardly on temperature in the 4.2–300 K range. The magnetic susceptibility and magnetization of strained Si and Ge single crystals were studied in [6], where it was shown that the strain changes substantially magnetization of the material. As a result, field dependences of MS appear, which were explained by magnetic ordering of carriers localized on crystal dislocations.

Magnetization of silicon [4] and silicon-germanium [7] whiskers was also shown to differ from that of bulk material. In particular, the diamagnetic susceptibility value for whiskers is less than MS of bulk material, which was explained by existence of paramagnetic centers therein [4, 7]. However, these studies were done only at room temperatures. In order to study the nature of magnetic centers in the whiskers, it is necessary to investigate their magnetic properties at low temperatures. This work deals with studies of magnetic properties of $Si_{1-\delta}Ge_{\delta}$ ($x = 0.01$–0.05) whiskers with boron concentrations ~$(2–8)\cdot10^{18}$ cm^{-3} near to the metal-insulator transition (MIT) in temperature range of 4.2–300 K. In particular, the magnetoresistance and magnetic susceptibility of the whiskers were investigated.

Si–Ge whiskers were grown by chemical transport reaction in a sealed tube [8]. In quartz tube, the following materials were loaded: silicon and germanium as growth materials; gold as the growth initiator; boron as the dopant and bromine as the transport agent. Temperature values in the evaporation zone and crystallization zone were 1000°C and 700–800°C, respectively. The investigated whiskers have diameters ranging from 20 to 50 μm. Ge content in $Si_{1-x}Ge_x$ whiskers was controlled by microprobe analysis and amounted 0.05, while boron concentrations n_B were about $(2–8)\cdot10^{18}$ cm^{-3}. To control the whisker contamination, Auger spectroscopy and mass spectral analysis was used. The analysis results indicate the absence of any impurities in the whiskers with concentration exceeding 10^{14} cm^{-3}. The whisker magnetic susceptibility was measured by Faraday method [9] in magnetic fields (0.3–4.0) kOe in temperature range 4.2–300 K. Before the measurements, samples were formed from the whiskers using the following way. The whiskers were packed in cylindrical glass tubes of 3 mm diameter that were then filled with beeswax. After that, the glass tube was removed from the samples. The experimental results show that magnetic susceptibility of beeswax is one order of magnitude lower than that of the whiskers. Nevertheless, the data were corrected every time for the magnetic contribution from beeswax. The measurement error did not exceed 5 %. The whisker magnetoresistance was measured in temperature range 4.2–77 K at magnetic fields of 0 to 14 T strength.

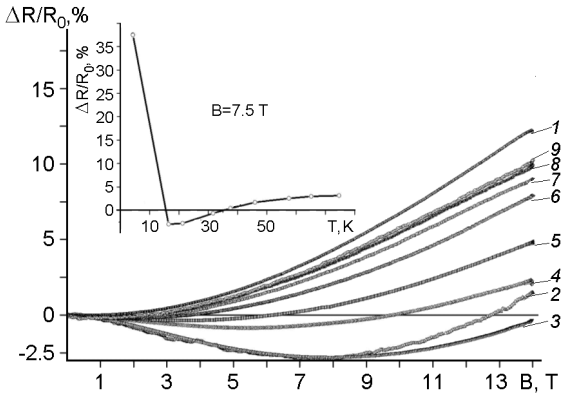

Fig. 1. Magnetoresistance of Si–Ge whisker with boron concentration $n_B = 2\cdot10^{18}$ cm^{-3}. Inset: temperature dependence of the whisker magnetoresistance. *1*–4.2: *2*–16.6; *3*–21; *4*–31.8; *5*–37.7; *6*–46; *7*–57.7; *8*–65.3; *9*–74.8 K.

Investigations of the whisker magnetoresistance show that the dependence of $\Delta R_B/R$ on magnetic field intensity differs substantially for the samples with various dopant concentrations. In the samples being at the metal side of MIT with boron concentration $(7–8)\cdot10^{18}$ cm^{-3}, the field dependence of magnetoresistance can be approximated by exponential law $\Delta R_B/R \sim \exp(B^n)$, where $n = 0.3$. In the samples being at the dielectric side of MIT with boron concentration $(3–5)\cdot10^{18}$ cm^{-3}, quadratic dependence of magnetoresistance on magnetic field intensity $\Delta R_B/R \sim B^2$ was observed. In typical semiconductor samples with boron concentration ~$2\cdot10^{18}$ cm^{-3}, negative magnetoresistance (NMR) (Fig. 1) was observed. The NMR value at $T = 20$ K amounted 2 %.

The presence of NMR in such samples can be explained by arising of antiferromagnetic exchange interaction during hopping conduction of holes (with activation energy ΔE_2) on delocalized states of upper Habbard band [10]. The temperature increase ($T > 30$ K) results in destruction of coupled hole pairs which results in disappearance of NMR.

The results of $Si_{0.95}Ge_{0.05}$<B> whiskers magnetic susceptibility measurements, in particular, field dependences of MS, for certain fixed temperatures 4.2 K, 77 K and 300 K, are presented in Fig. 2. The whisker magnetic susceptibility is seen to change the sign at increase of magnetic field and saturates in the field exceeding 4 kOe ($T = 296$ K). It should be noted that the whisker magnetic susceptibility differs substantially from bulk Si–Ge ($\chi = -0.116\cdot10^{-6}$ at room temperature). The difference consists in two

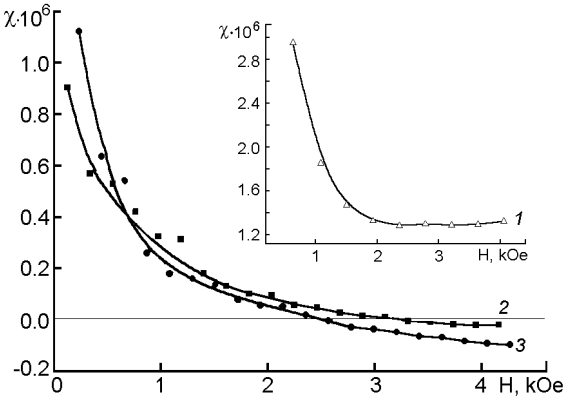

Fig. 2. Field dependences of magnetic susceptibility of $Si_{0.95}Ge_{0.05}$<B> whiskers at fixed temperatures *1* – 4.2 K, *2* – 77 K; *3* – 296 K.

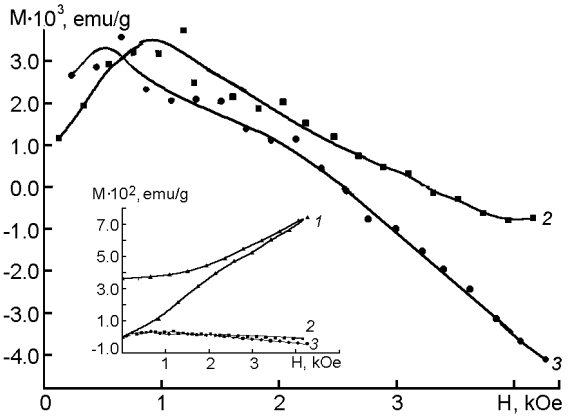

Fig. 3. Magnetization of $Si_{0.95}Ge_{0.05}$<B> whiskers for certain fixed temperatures: *1* – 4.2; *2* –77; *3* – 296 K.

main points: (i) the saturated value $\chi = -0.1 \cdot 10^{-6}$ for the whiskers is lower than that of bulk Si–Ge; (ii) strong field dependence $\chi(H)$ is observed in the whiskers, which indicates the presence of magnetic interaction between centers therein.

Since the magnetization is connected with the magnetic susceptibility by simple relationship $M = \int \chi dH$, it is easy to obtain the corresponding dependences of $M(H)$. The result of such mathematical transformation at room and liquid nitrogen temperature is provided in Fig. 3. The results in Fig. 3 are likely explained by appearance of magnetic ordering between the centers in crystals at low temperatures [4, 7]. This is apparently supported by observed hysteresis in the field dependence of magnetization M at 4.2 K with coercivity about 1 kOe (see Fig. 3).

Si–Ge solid solution is a diamagnetic material with constant (independent of magnetic field intensity) magnetic susceptibility value at room temperature. The whisker MS peculiarities, in particular, appearance of a paramagnetic component in MS, indicate the presence of paramagnetic centers in the whiskers. The field dependences of $\chi(H)$ as well as observed hysteresis at low temperature can be explained by magnetic-doublet or exchange interaction between these centers in the crystals [11].

The above behavior of magnetic susceptibility can be explained by either impurity or defects present in the whiskers. Let these two possible reasons be considered.

Si–Ge whiskers were doped during the growth by B and Au impurities. These two impurities are known to make diamagnetic contribution to magnetic susceptibility. The observed saturation value of $\chi = -0.1 \cdot 10^{-6}$ in high magnetic fields (Fig. 2), which includes contributions from silicon lattice and impurity subsystem, is shifted towards paramagnetic side as compared to bulk Si–Ge. This fact indicates the existence of paramagnetic centers in the whiskers in concentrations exceeding B and Au ones. However, the results of the whisker investigation by microprobe analysis (CAMEBAX) show that those contain only residual (for this analysis) concentrations $n_B \sim 2 \cdot 10^{18}$ cm^{-3}. No concentrations of others impurities were revealed in the whiskers. The accuracy of microprobe analysis is too low for such investigations. Therefore, we controlled the whisker composition by mass-spectral analysis and did not establish any others impurities in the whiskers. The results of the whisker surface investigation by Auger-spectroscopy indicate the existence of very thin (a few nm) dense layer of SiO_2 as well as C and N atoms. All these materials are not magnetic impurities. Therefore, the observed behavior of the whisker magnetic susceptibility cannot be explained by impurity contribution.

As was shown before, the whisker is known to be a "heterostructure" with crystalline core of bulk material and porous shell [12]. Besides, EPR data show that porous shell contains a great amount of dangling bonds. Existence of dangling bonds in porous envelope of Si–Ge whiskers seems to be consistent with a difference of the whisker MS from that of bulk material. Dangling bonds are known to be paramagnetic centers. Therefore, their existence explains in good manner the saturation value of $\chi = -0.1 \cdot 10^{-6}$ at high magnetic fields

(Fig. 2, T = 296 K). The field dependence of magnetic susceptibility indicates an interaction of dangling bonds. Really, the dangling bonds are located in interstices, dimensions of which are substantially less than the whisker diameter (d≈300–500 nm). Such dimensions can be of about 3–50 nm. So, there are appropriate distances for magnetic interaction of dangling bonds located in an interstice.

To determine the nature of paramagnetic centers, we have verified the Curie law. In particular, we have presented the temperature dependence of magnetization as a function of H/T at fixed temperatures (Fig. 4). The obtained data for three temperatures are seen to fit not to one curve as it should be for an explicitly paramagnetic material [11]. The magnetic centers can be supposed to arise due to interaction of magnetic orbital moments of dangling bonds with delocalized impurity states of upper Habbard band in heavily doped Si–Ge with boron concentration close to MIT. Hence, similar to amorphous silicon doped with rare-earth impurities [11], magnetic polarons are likely formed in a nanoporous shell of heavily doped whiskers. Such magnetic states exist only at low temperature (4.2–30 K) and are broken at its elevation. The presence of magnetic polarons results in arising antiferromagnetic exchange interaction [11]. As a result, two things take place: deviation from Curie law for magnetic susceptibility and existence of negative magnetoresistance in the investigated samples. However, confirmation of this assumption as well as distinct determination of magnetic interaction nature in the whiskers demands further investigations.

To conclude, the magnetoresistance and magnetization of $Si_{0.95}Ge_{0.05}$<B> whiskers has been measured in wide temperature range 4.2–300 K in magnetic fields up to 140 and 4 kOe, respectively. The experimental data on magnetization and magnetic susceptibility indicate the existence of substantial magnetic ordering in $Si_{0.95}Ge_{0.05}$<B> whiskers, the magnitude of which increases with temperature decrease. The observed behavior of magnetic properties is not connected with impurity content

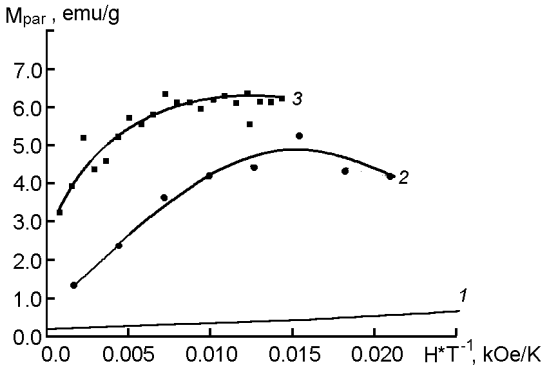

Fig. 4. Magnetization of $Si_{0.95}Ge_{0.05}$<B> whiskers at different temperatures: *1*–4.2; 2–77; *3* –296 K as function of magnetic field intensity and temperature.

of the whiskers. Existence of dangling bonds in porous envelope of Si–Ge whiskers is likely consistent with a MS difference between the whiskers and the bulk material.

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Магнітоопір та магнітна сприйнятливість легованих ниткоподібних кристалів Si–Ge

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Визначено магнітопір та магнітну сприйнятливість (МС) ниткоподібних кристалів (НК) Si–Ge<B> у діапазоні температур 4,2–300 К у магнітних полях до 140 кЕ та 4,0 кЕ, відповідно. Отримані результати мають дві особливості: парамагнітний вклад у намагніченість у МС та нелінійну залежність намагніченості від магнітного поля. Ці факти вказують на наявність антиферомагнітного впорядкування у НК. Наявність гистерезису намагніченості при 4,2 К підтверджує це припущення. Обговорюються можливі причини виявленого ефекту.