MAGNETIC SUSCEPTIBILITY OF WHISKERS OF $\mathbf{Si_{0.95}Ge_{0.05}}$

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The investigation of magnetic susceptibility (MS) of $Si_{1-x}Ge_x(x = 0.05)$ whiskers at $T = 300$ K in the magnetic fields of 0.3–5 kOe is carried out. The submicron quasicylindrical whiskers ($0.1 < d < 3$ μm) and needdle-like ones ($3 < d < 50$ μm) are studied. It is established that the behavior of MS for whiskers essentially differs from that of the bulk material, which is explained by the features of their crystalline structure and chemical composition. A theoretical model describing the obtained experimental results is suggested, and it is proved that they are well-grounded within this model.

1. Introduction

Recently, the study of low-dimension structures has attracted the growing interest. In particular, a number of size effects in submicron whiskers of Si and Si–Ge was revealed in the case where their diameters are decreased: one observes a change of the lattice constant [1], a displacement of the fundamental adsorption edge, and the appearance of a visible luminescence similar to the luminescence of porous silicon [2]. In whiskers of silicon, the significant variations in MS depending on the diameter of these crystals were observed [3, 4]. Therefore, it is of interest which peculiarities of magnetic properties will occur in whiskers of solid solutions of Si–Ge.

2. Experimental Results and Calculations

Whiskers of Si–Ge were grown by the method of chemical transport reactions in a closed bromide system with the use of alloying admixtures (Pt, B, and Au) [5]. The content of Ge in the solid solution Si–Ge was controlled by the method of microprobe analysis and was $x = 0.05$. The studies of the growth of whiskers showed a change in the mechanism of growth on the transition from needle-like crystals to crystals of submicron diameters. Quasicylindrical whiskers of submicron diameters are formed by the vapor–liquid–crystal mechanism [6], whereas needle-like whiskers of great diameters are formed by the vapor–crystal mechanism [3]. In these casee, the morphology and structure of crystals are changed. For example, submicron whiskers are distinctive "heterostructures" that are composed from a monocrystalline core and a porous nanoshell [7]. Needle-like whiskers ($3 < d < 50$ μm) are single crystals with well-manifested faceting.

The measurement of MS of specimens was carried out by the Faraday method [8] in magnetic fields of (0.3–5.0) kOe at $T = 300$ K. The maximum error of measurements was at most 3%. Prior to the measurement, whiskers were placed on a Si plate and glued with an alcoholic solution of glue BF-2 (1–2%). It was experimentally established that the influence of the gluing of crystals did not exceed the error of measurements.

In Fig. 1, we present MS of whiskers of Si–Ge of 0.1–50 μm in diameter versus the external magnetic field strength. The diameters of specimens are shown in inserts in the figure. It is seen that $\chi(H)$ for specimens *1, 2, 5*, and *6* depends nonlinearly on the magnetic field strength, which especially distinguishes it from such a dependence in bulk crystals. We note that the diamagnetism of specimens *3* and *4* is greater than that of bulk crystals of Si ($\chi_L^{\mathrm{Si}} = -11.6 \times 10^{-8}$ cm^3/g) and Ge ($\chi_L^{\mathrm{Ge}} = -11.2 \times 10^{-8}$ cm^3/g).

The experimental dependences $\chi(H)$ can be considered as the sum of two components: the component (χ^{ind}) independent of the field and the dependent one (χ^{ord}) that is related to the ordering of magnetic centers in a crystal:

$$\chi(H) = \chi^{\text{ord}}(H) + \chi^{\text{ind}}. \tag{1}$$

The component χ^{ind} corresponds to MS under saturation that is practically attained in our case in magnetic fields of 4–5 kOe (Fig. 1).

The component χ^{ind} includes the susceptibility of the lattice (χ_L) and the paramagnetic component (χ^{par}) independent of the magnetic field strength:

$$\chi^{\text{ind}} = \chi^{\text{par}} + \chi_L. \tag{2}$$

The experimental studies of MS of the crystal lattices of continuous solid solutions $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ and the analysis of MS of the lattices of binary semiconductors $\text{A}^{\text{II}}\text{B}^{\text{VI}}$ and $\text{A}^{\text{III}}\text{B}^{\text{V}}$ and their solid solutions allow us to assert that χ_L is a linear function of their composition [9]. Since $\chi_L^{\text{Si}} = -11.6 \times 10^{-8}$ cm^3/g and $\chi_L^{\text{Ge}} = -11.2 \times 10^{-8}$ cm^3/g, the solid solution $\text{Si}_{0.95}\text{Ge}_{0.05}$ should be characterized by $\chi_L^{\text{Si}_{0.95}\text{Ge}_{0.05}} = -11.58 \times 10^{-8} \approx -11.6 \times 10^{-8}$ cm^3/g. But it is unknown whether this is valid in the case of whiskers.

We pay attention to the fact that MS of crystal *3* is independent of the magnetic field strength. As for crystal *4*, whose MS does not also depend on H, it has a close value of MS. We accept the value of diamagnetic susceptibility of crystal *3* as the susceptibility of the crystal lattice and will consider that MS of the lattices of the whiskers of Si-Ge under study $\chi_L = -17.2 \times 10^{-8}$ cm^3·g^{-1}. Then the decrease in the diamagnetism of whiskers can be explained by 1) increase in the paramagnetism independent of the magnetic field (χ^{par}) and 2) increase in the paramagnetism that depends on H ($\chi^{\text{ord}}(H)$). In the first case, the paramagnetism is caused by dispersed paramagnetic centers or by the centers which are located in aggregates with less density and do not transit into a magnetically ordered state at $T \geq 290$ °C. In the second case, the paramagnetism depends on the magnetic field strength in the interval $0 < H \leq 5$ kOe. In view of the character of the dependence $\chi^{\text{ord}}(H)$, we draw conclusion about its superparamagnetic nature. This fact is also confirmed by the absence of a hysteresis for the whiskers under study. As a physical reason for the appearance of this paramagnetism, we may consider the creation of "quasiferromagnetic" aggregates (clusters) in whiskers. The behavior of these aggregates is similar to the Langevin paramagnetism of atoms possessing a magnetic moment. The main difference consists in that the magnetic moment of such aggregates can be by 10^3-10^5 times greater than the magnetic moments of individual atoms.

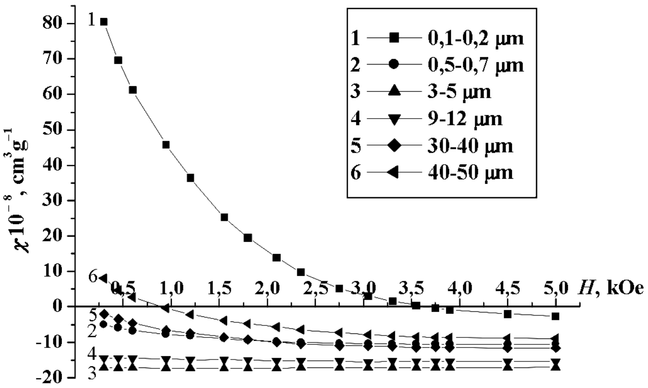


Fig. 1. Magnetic susceptibility of whiskers of $\text{Si}_{1-x}\text{Ge}_x$ versus the external magnetic field strength

Taking the above assumptions and remarks into account, the formula for the observed MS of whiskers of Si-Ge can be presented in the following form:

$$\chi(H) = \chi^{\text{ord}}(H) + \chi^{\text{par}} + \chi_L =$$

$$= N_{\text{cl}} m_{\text{cl}} L'\left(\frac{m_{\text{cl}} H}{kT}\right) + \chi^{\text{par}} + \chi_L, \tag{3}$$

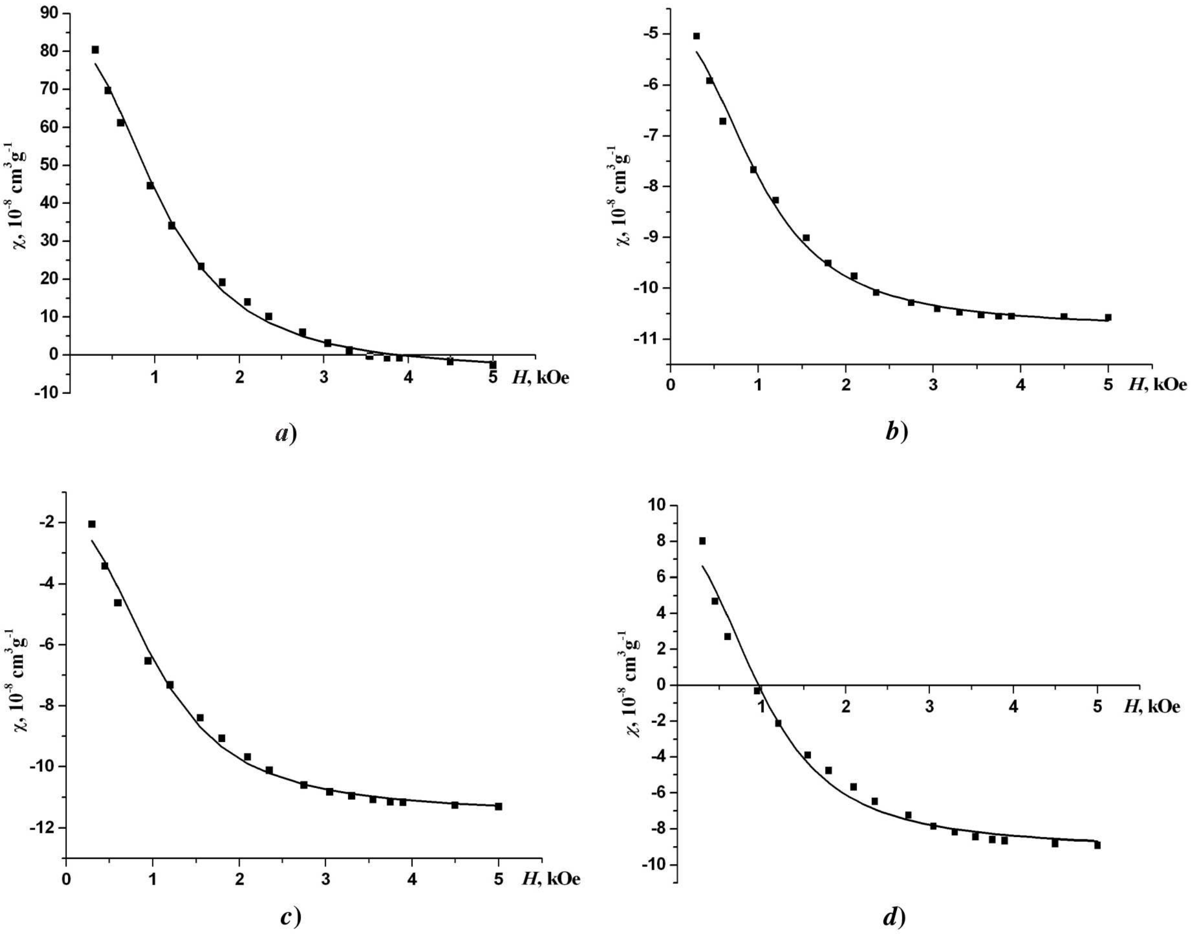
where N_{cl} – concentration of magnetically ordered clusters; m_{cl} – magnetic moment of one of such clusters (in the first approximation, we consider that the magnetic moments of clusters are identical); $L'(x)$ – derivative of the Langevin function, k – Boltzmann constant, T – temperature, $m_{\text{cl}} = N_0 \mu_{\text{B}} g \sqrt{s(s+1)}$, where N_0 – number of paramagnetic centers in a single magnetic cluster, μ_B – Bohr magneton, g – g-factor (in estimates, we take $g = 2$), and s – spin of a paramagnetic center entering the cluster (in estimates, we take $s = 1/2$). Hence, Eq. (3) takes the form

$$\chi(H) = N_{\text{cl}} N_0 \mu_{\text{B}} g \sqrt{s(s+1)} \times$$

$$\times \left(\frac{N_0 \mu_{\text{B}} g \sqrt{s(s+1)}}{\left(\sinh\left(\frac{N_0 \mu_{\text{B}} g \sqrt{s(s+1)}}{kT} H\right)\right)^2 kT} + \right.$$

$$\left. + \frac{kT}{N_0 \mu_{\text{B}} g \sqrt{s}(s+1) H^2} \right) + \chi^{\text{par}} + \chi_L. \tag{4}$$

By fitting the experimental curves *1, 2, 5* and *6* with the use of function (4), we can estimate the quantities N_0 and N_{cl}. The obtained results are given in Fig. 2.



a)

b)

c)

d)

Fig. 2. Fitting of experimental data on $\chi(H)$ by (4): *a* – curve *1* – 0.1–0.2 μm, $\chi_L = -17.2 \times 10^{-8}$ cm^3·g^{-1}, $\chi^{\rm par} + \chi_L = -5.0 \times 10^{-8}$ cm^3·g^{-1}, $\chi^{\rm par} = 12.2 \times 10^{-8}$ cm^3·g^{-1}, $N_0 = 4.8 \times 10^3$ cm^{-3}, $N_{\rm cl} = 1.8 \times 10^{10}$ cm^{-3}; *б* – curve *2* – 0.5–0.7 μm, $\chi_L = -17.2 \times 10^{-8}$ cm^3·g^{-1}, $\chi^{\rm par} + \chi_L = -10.8 \times 10^{-8}$ cm^3·g^{-1}, $\chi^{\rm par} = 6.4 \times 10^{-8}$ cm^3·g^{-1}, $N_0 = 5.3 \times 10^3$ cm^{-3}, $N_{\rm cl} = 1.0 \times 10^9$ cm^{-3}; *в* – curve *5* – 30–40 μm, $\chi_L = -17.2 \times 10^{-8}$ cm^3·g^{-1}, $\chi^{\rm par} + \chi_L = -11.6 \times 10^{-8}$ cm^3·g^{-1}, $\chi^{\rm par} = 5.6 \times 10^{-8}$ cm^3·g^{-1}, $N_0 = 5.0 \times 10^3$ cm^{-3}, $N_{\rm cl} = 1.8 \times 10^9$ cm^{-3}; *g* – curve *6* – 40–50 μm, $\chi_L = -17.2 \times 10^{-8}$ cm^3·g^{-1}, $\chi^{\rm par} + \chi_L = -9.2 \times 10^{-8}$ cm^3·g^{-1}, $\chi^{\rm par} = 8.0 \times 10^{-8}$ cm^3·g^{-1}, $N_0 = 5.2 \times 10^3$ cm^{-3}, $N_{\rm cl} = 3.0 \times 10^9$ cm^{-3}

In Fig. 3, we show the experimental data and the results of the fitting of the field-independent components of MS, $\chi^{\rm ind}(d)$, of whiskers of $\rm Si_{0.95}Ge_{0.05}$ for specimens with various diameters.

It is seen that the diamagnetism of both submicron quasicylindrical (*1–3*) and needle-like whiskers (*4–6*) exceeds that of bulk crystals of Si and Ge by more than 40% (the dashed line), when their diameters approach the interval $2 < d < 6$ μm.

3. Discussion of Experimental Results

It is worth noting the dependence of MS $\chi^{\rm ind}$ of whiskers of $\rm Si_{0.95}$ $\rm Ge_{0.05}$ on their diameter (Fig. 3). The increase in the diamagnetism (specimens *3* and *4*) as compared with that of bulk Si and Ge falls in the interval of diameters of 2–6 μm, where one observes the maximum of the dependence of the growth rate of whiskers on the diameter, v (d)) [10]. The observed peciliaritity cannot be related to the content of admixtures in the crystals. It is known from electrophysical studies of whiskers [11] that the increase in a diameter of submillimeter crystals is accompanied by an increase in the concentration of platinum (to 10^{17}–10^{18} cm^{-3}) which is a paramagnetic admixture. As diameters decrease from 50 down to 1–5 μm, the concentration of boron increases from 10^{16}–10^{17} to $2{\times}10^{19}$ cm^{-3}, whose MS is diamagnetic (χ (B) $=$ -70×10^{-8} cm^3·g^{-1}). However, according to [12], the

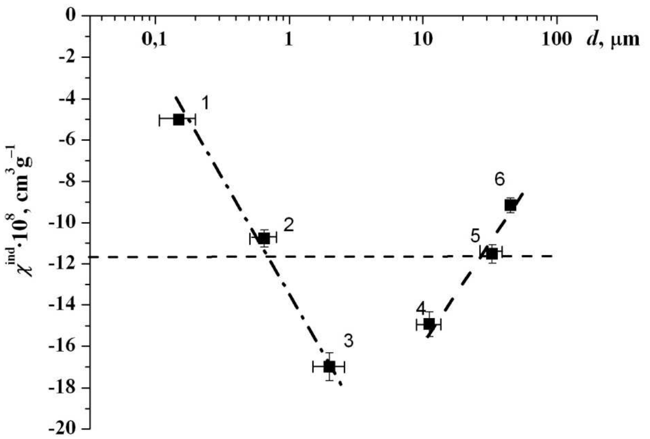


Fig. 3. Magnetic susceptibility χ^{ind} of whiskers of $\mathrm{Si}_{0.95}\mathrm{Ge}_{0.05}$ versus their diameter. The numbers at points are the numbers of specimens

increase in the concentration of boron in Si specimens to 5×10^{19} cm^{-3} does not practically influence the change of MS of crystals at room temperature. Hence, the revealed growth of the diamagnetism of specimens *3* and *4* as compared with that of a bulk material cannot be explained by available admixtures. The above-formulated assumption that the values of the diamagnetic susceptibility of specimen *3* can be taken as MS of the lattice of whiskers under study ($\chi_L = -17.2\times10^{-8}$ cm^3·g^{-1}) is based also on the fact the dependence $\chi(H)$ for this specimen is linear. Hence, the component $\chi^{\mathrm{ord}}(H)$ is absent. With regard for the fact (as seen from Fig. 1) that the paramagnetic contribution χ^{par} is proportional to the superparamagnetic one χ^{ord} (at $H = 0$), we may conclude that this specimen does not contain noninteracting paramagnetic centers.

Thus, we assune that the value of χ_L remains stable in all specimens, and the registered decrease in the diamagnetism is caused both by an increase in the paramagnetism, χ^{par}, independent of the magnetic field and by the superparamagnetism, $\chi^{\mathrm{ord}}(H)$.

We now consider the peculiarities of submicron quasicylindrical ($0.1 < d < 3$ μm) and submillimeter needle-like ($3 < d < 50$ μm) whiskers of $\mathrm{Si}_{0.95}\mathrm{Ge}_{0.05}$ in more details.

MS of submicron crystals can be explained by peculiarities of their structure. As was mentioned above, such crystals are natural heterostructures composed from the central part, a monocrystalline core, and a porous nanoshell (Fig. 4) [7]. The shell structure is similar to the crystalline structure of porous silicon. This is indicated by a luminescence in the visible region registered from both porous silicon and submicron whiskers of Si–Ge. As seen from Fig. 4, the sizes of pores are at most 10 nm. We may assume that the porous shell is responsible for the specific behavior of MS of submicron whiskers.

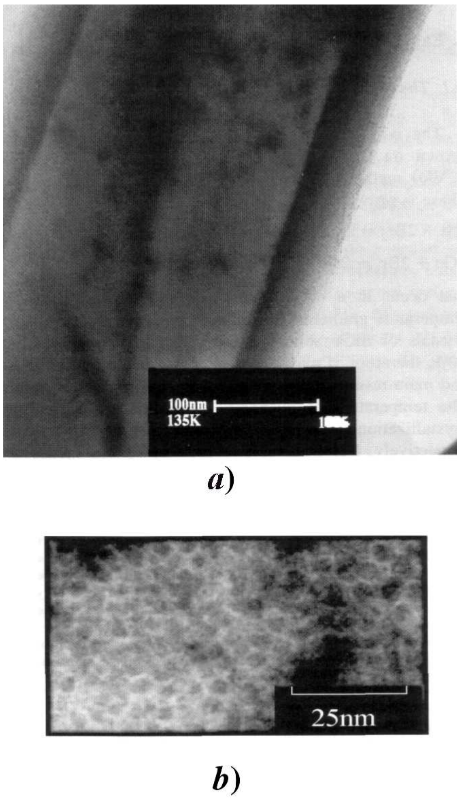
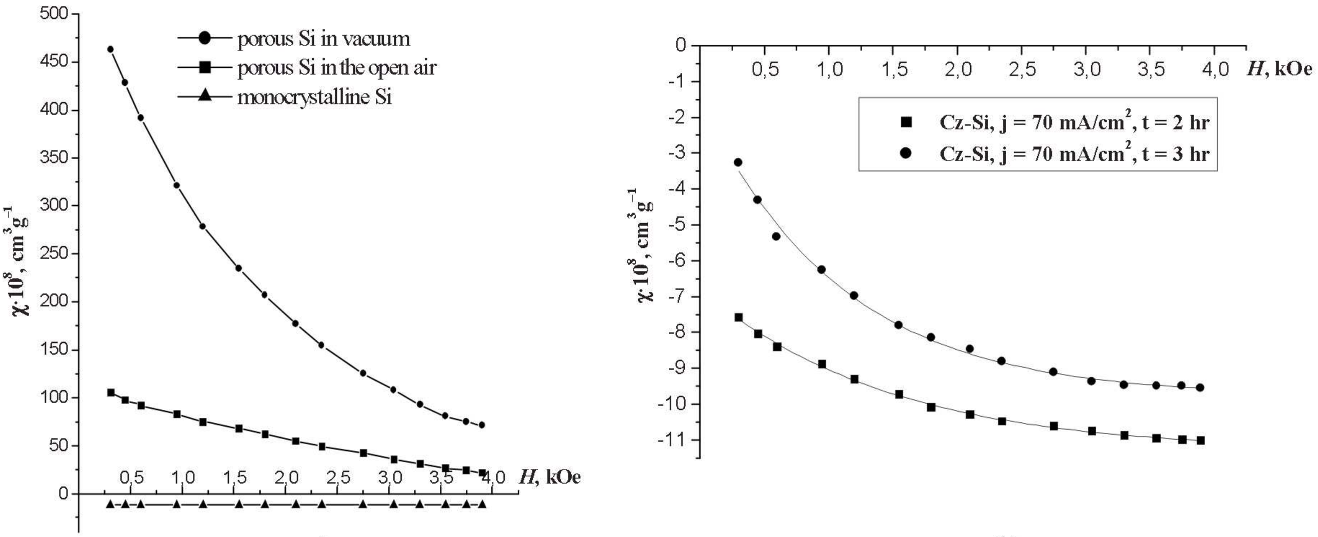


Fig. 4. Crystal structure of submicron whiskers (*a*) and a porous nanoshell (*b*) [7]

This yields the necessity to study the MS of porous silicon. The results obtained by us are given in Fig. 5. We studied porous silicon in a vacuumized ampoule (Fig. 5,*a*, curve *1*) and in air (Fig. 5, 5,*a*, curve *2*). The decrease of the paramagnetism in air is related, obviously, to the partial passivation of broken bonds.

As seen, the MS of porous silicon is paramagnetic and strongly depends on the magnetic field strength. It is worth noting that the dependence $\chi(H)$ of porous silicon studied in air is close to that of submicron whiskers of 0.1–0.2 μm in size. We indicate the presence of a porous shell on the surface of a bulk specimen of silicon. This shell is formed by etching in a special etchant on the passage of a current and also leads to both a decrease in the diamagnetism and the appearance of nonlinear dependences $\chi(H)$ (Fig. 5,*b*). Moreover, the thicker the porous shell (the longer the etching), the greater the effect.



***a*)** ***b*)**

Fig. 5. Magnetic susceptibility of porous Si (*a*) and bulk Si with porous surface (*b*) versus the magnetic field strength

The validity of our assumptions is proved by the results of EPR of submicron whiskers, which indicate the presence of a quite significant concentration of broken bonds $\sim 10^{14}$ cm^{-2} on their surface [13]. Since the specific area of the surface of specimens increases, as their transverse sizes decrease, the total concentration of broken bonds in this case grows, by causing the increase in the concentration of paramagnetic centers in crystals and, respectively, the decrease in the diamagnetic component χ^{ind} (Fig. 3).

MS of submillimeter crystals of sizes more than 7 μm that are homogeneous single crystals is explained by the presence of admixtures entering the crystal during its growth.

As was mentioned above, the growth of the diameter of crystals is associated with increase in the concentration of platinum (of the order of 10^{17}–10^{18}cm^{-3}) [11] which can exceed the limiting value of solubility of Pt in Si $N_{\mathrm{sol}} \approx 7 \times 10^{16}$ cm^{-3}. Platinum is a paramagnet, (χ(Pt) $= +110 \times 10^{-8}$ cm^{3}g^{-1}), and it can lead to an increase in the paramagnetic component of MS. On the other hand, on a high content of Pt, macroprecipitates Si–Pt are formed. This causes significant mechanical stresses. As a result, edge dislocations (paramagnetic D-centers) with broken bonds are created on the interface between precipitates and the Si matrix.

Based on the proposed model, we may assume that the field dependences of MS of whiskers can be explained by the fact that a part of paramagnetic centers creates nanoclusters which have the superparamagnetic nature. We note that analogous nonlinearities were observed by us [14] in crystals of Si alloyed with gadolinium.

On the basis of the theoretical modeling, we have established (see Fig. 2) that, for all specimens, the number of paramagnetic centers in a cluster is near (5000 ± 300) cm^{-3}, and the concentrations of superparamagnetic clusters vary in the limits of 10^9–10^{10} cm^{-3}. It seems that the obtained estimates are quite reasonable.

4. Conclusions

We have established that the behavior of MS of whiskers of $\mathrm{Si}_{0.95}\mathrm{Ge}_{0.05}$ with various diameters is significantly different from that of MS of a bulk material, for which $\chi \approx -11.6 \times 10^{-8}$ cm^3/g), and does not depend on the magnetic field strength. In submicron crystals, the decrease in their diameters from 3–1 down to 0.1 μm leads to both the growth of the paramagnetic component of MS and the appearance of a nonlinearity in the dependence of MS on the magnetic field strength. This is possibly related to the presence of a porous nanoshell on the surface of these specimens. In the case of submillimeter crystals, we have registered the enhancement of both the paramagnetism and the nonlinearity of $\chi(H)$ with increase in their diameters, which can be caused by the formation of macroprecipitates Si–Pt.

By analyzing the nonlinear dependence $\chi(H)$, we may assume that a part of paramagnetic centers forms nanoclusters that have the superparamagnetic nature. Based on the proposed model, we have estimated the concentration of superparamagnetic clusters in the limits of 10^9–10^{10} cm^{-3} and the number of paramagnetic centers in a single cluster of about (5000 ± 300) cm^{-3} for all specimens.

We have established that, in whiskers of $\mathrm{Si}_{0.95}\mathrm{Ge}_{0.05}$ with diameters of 2–6 μm, the contribution from the superparamagnetic and paramagnetic components is minimum, whereas the diamagnetism is somewhat greater than that in a bulk material and, in the frame of the proposed model, is invariable for all specimens under study.

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МАГНІТНА СПРИЙНЯТЛИВІСТЬ НИТКОПОДІБНИХ КРИСТАЛІВ $\mathrm{Si}_{0,95}\mathrm{Ge}_{0,05}$

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Резюме

Проведено дослідження магнітної сприйнятливості (МС) ниткоподібних кристалів (НК) $\mathrm{Si}_{1-x}\mathrm{Ge}_x (x = 0,05)$ при $T = 300$ К в магнітних полях 0,3–5 кЕ. Досліджено субмікронні квазіциліндричні (діаметром $0,1 < d < 3$ мкм) і субміліметрові голкоподібні (діаметром $3 < d < 50$ мкм) ниткоподібні кристали. Встановлено, що поведінка МС НК істотно відрізняється від МС об'ємного матеріалу, що пояснено особливостями їх кристалічної структури та хімічним складом. Запропоновано теоретичну модель, яка описує одержані експериментальні результати, і показано, що в її межах вони є обґрунтованими.