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Low temperature behaviour of the giant magnetoresistivity in CoFeB–SiO_n granular composites

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Abstract

Giant magnetoresistivity (GMR) at different temperatures as well as magnetization processes were studied in amorphous granular composites $(Co_{41}Fe_{39}B_{20})_x(SiO_n)_{100-x}$ over a wide concentration range ($20 \leqslant x$, at.% $\leqslant 59$). Magnetoresistivity of the composites with large dielectric content (below a percolation threshold) is enhanced on cooling down to 77 K and reaches 7% in $(Co_{41}Fe_{39}B_{20})_{30}(SiO_n)_{70}$. The observed GMR enhancement directly correlates with the rise of the relative change of the composites magnetization ($[m_{77} - m_{300}]/m_{300}$) occurring on temperature reduction. The temperature dependence of the composite's GMR exhibits a clear maximum in the vicinity of 77 K if a wider temperature range (2–300 K) is considered. The difference between the GMR values measured at 77 and 2 K is one order of magnitude. Strong Coulomb blockade is observed in this composite at low temperature.

1. Introduction

Granular nanocomposites (cermets) are an artificial material consisting of nano-sized metal granules embedded in a dielectric matrix. The attention to the composites is determined by the giant magnetoresistivity (GMR) observed in such a class of materials (up to 10% at room temperature) [1]. In spite of the relatively high values of GMR, which can be obtained in single artificial tunnel junctions (above 20% at room temperature) [2], interest in the granular materials remains quite high because there are real problems in the preparation and use of junctions [1], while the composites are free of them. The best known and studied composite

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is Co–Al–O [1, 3, 4] although many other systems have also been investigated: Fe–Al–O [5], Ni–Si–O [6], Co–Si–O [7], Fe–Si–O [8] and so on. Analysis of the published data indicates that all known cermets contain a simple metal phase (single-element granules or two-element granules, for example Co–Fe in a CoFe–HfO composite [9]). In such a case, it is not possible (or is very difficult) to change the physical properties of the metal nano-granules smoothly and to perform requirement properties of the whole composite accordingly. Besides that, the published data concerning the concentration dependence of composite properties and changes of the properties with variation in temperature is also insufficient. Therefore, the composites with granules formed from complicated metal alloys (soft magnetic material Co–Fe–B) have been chosen for investigation [10]. The GMR and magnetic properties of the composites were studied for a wide concentration region and at different temperatures.

2. Experimental procedure

The film samples of granular composites have been prepared by ion-beam sputtering of a composite target under a low pressure argon atmosphere (0.067 Pa). The target was made from the metal base (Co–Fe–B alloy) and several quartz plates on its surface. Changing the number of the plates provided a change of the metal/dielectric ratio in the composite. The distance between target and substrate was 140 mm and therefore the composition dispersion in the growing film was very small. The substrates were not cooled during deposition but the temperature did not exceed 370 K. Deposition of the material was carried out on the KCl single-crystal substrates for transmission electron microscopy (TEM). The glass ceramic substrates were used for other measurements. The samples sputtered on the glass ceramic surface had a thickness of about 3 μm. The composition of the samples was determined by x-ray electron-beam microanalysis with energy dispersion directly after deposition. Magnetoresistivity of the composites was calculated according to expression $(R_H - R_0)/R_0$, where electrical resistance (R) was measured by a two-probe technique in a stabilized current mode and current-in-plane geometry. A magnetic field was also applied parallel to the sample's surface and parallel to the current flow. The bronze probes were used for electrical measurements and the contact pots were stabilized by In–Ga solder. Magnetic properties of the composites were studied by a vibrating sample magnetometer with applied field parallel to the sample's surface.

3. Results and discussion

Samples of six cermets with different metal/dielectric ratios, covering a wide concentration region, were prepared for investigation (see table 1). According to the TEM study all composites containing silicon oxide were heterogeneous with nanogranular structure (see figure 1). One should note that the film thickness in the case of the TEM investigations is approximately 50–70 nm, so the obtained 2D TEM image actually displays the projection of all granules, which are in the 3D film, on the plane. Therefore, it is quite easy to determine the granule diameter, but determination of the intergranule distance is problematical. Nevertheless, it is obvious that an increase of the dielectric phase content leads to a considerable reduction of the granule diameter (see table 1 and figure 1).

It is known that the maximum values of the GMR should be in those composites that are close to the electrical percolation threshold [11]. The electrical percolation threshold corresponds to the concentration where the composite conductivity is changed from non-metallic to metallic. In other words, when the amount of the metal phase is so large, that continuous channels begin to be formed from metal granules and electrons have the possibility to pass via the conducting channels through the whole material. Analysis of

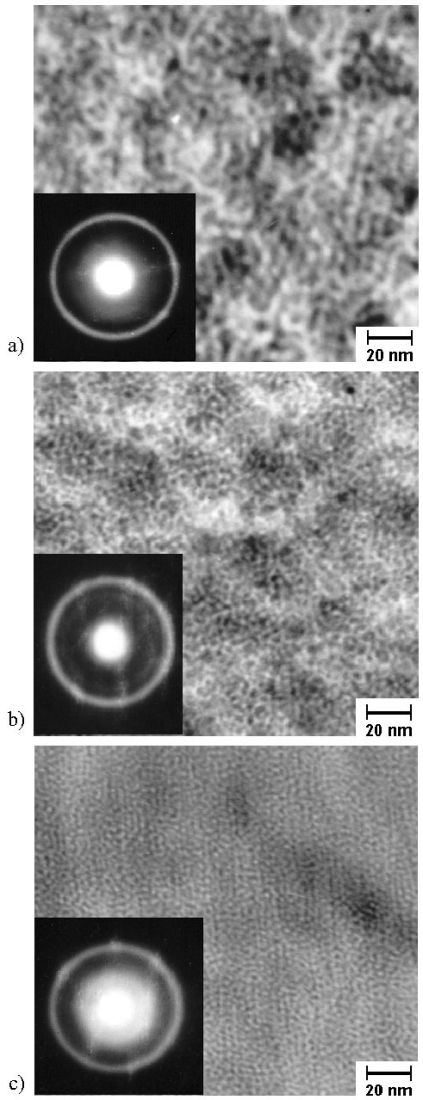

Figure 1. TEM images and diffraction picture (insets) of $(Co_{41}Fe_{39}B_{20})_x(SiO_n)_{100-x}$ granular composites: (a) $(Co_{41}Fe_{39}B_{20})_{59}(SiO_n)_{41}$; (b) $(Co_{41}Fe_{39}B_{20})_{43.5}(SiO_n)_{56.5}$; (c) $(Co_{41}Fe_{39}B_{20})_{30}(SiO_n)_{70}$. The dark regions are the metal granules, while the light regions are the silicon oxide.

the temperature dependence of the composite's resistivity for different $(Co_{41}Fe_{39}B_{20})/SiO_n$ ratios [10] and concentration dependence of the composite's magnetoresistivity (figure 2) allows us to conclude that electrical percolation takes place in the $(Co_{41}Fe_{39}B_{20})_x(SiO_n)_{100-x}$ composites when the concentration of the metal phase is close to 45 at.%. This value is in good agreement with the published data for $Fe_x(SiO_2)_{100-x}$, $Co_x(SiO_2)_{100-x}$ and $Ni_x(SiO_2)_{100-x}$ composites [6, 11].

The GMR is associated with tunnelling of spin-polarized electrons between ferromagnetic granules [12, 13]. The probability of electron tunnelling from one to another neighbouring granule depends on the mutual orientation of the granule's magnetic moment [1, 14], it is

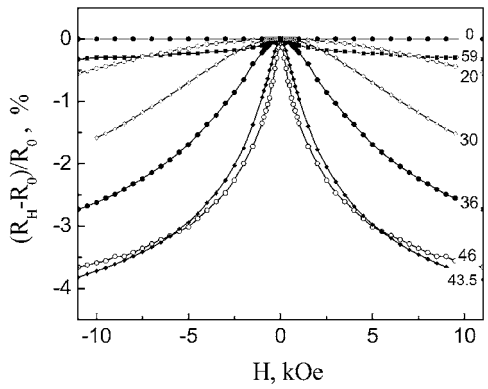

Figure 2. GMR of the $(Co_{41}Fe_{39}B_{20})_x(SiO_n)_{100-x}$ amorphous composites at 300 K. The number near the curves indicates the metal phase concentration (x) in at.%.

Table 1. Composition and structural features of the CoFeB–SiO_n composites as well as values of the GMR.

Composition (at.%) $1.3 < n < 1.9$	Structure	Average granules diameter (nm)	$(R_H - R_0)/R_0$ at 300 K (%) in 11 kOe
$Co_{41}Fe_{39}B_{20}$	Amorphous	Homogeneous alloy	0
$(Co_{41}Fe_{39}B_{20})_{59}(SiO_n)_{41}$	Amorphous	6–8	0.35
$(Co_{41}Fe_{39}B_{20})_{46}(SiO_n)_{54}$	Amorphous	—	3.77
$(Co_{41}Fe_{39}B_{20})_{43.5}(SiO_n)_{56.5}$	Amorphous	4–5	3.99
$(Co_{41}Fe_{39}B_{20})_{36}(SiO_n)_{64}$	Amorphous	—	3.06
$(Co_{41}Fe_{39}B_{20})_{30}(SiO_n)_{70}$	Amorphous	2–3	1.88
$(Co_{41}Fe_{39}B_{20})_{20}(SiO_n)_{80}$	Amorphous	—	0.63

high when the moments are parallel and is small when the moments are not parallel. On the other hand, it is known that the macroscopic magnetic state of granular metal/dielectric composites is superparamagnetic at room temperature [6, 15, 21, 22]. Therefore, the granules are not interacting with each other and reorientation of their magnetic moments is independent. The applied magnetic field aligns the granule moments and thereby influencing the tunnelling probability and composite resistance, respectively. Theoretically, it was shown that magnetoresistivity of granular composites (as defined by $[R_H - R_0]/R_0$) is given by $P^2(M/M_S)^2$, where P is a scaling factor, related to the spin polarization, while M and M_S are the magnetization and saturated magnetization, respectively [16]. In the $(Co_{41}Fe_{39}B_{20})_x(SiO_n)_{100-x}$ amorphous composites this relation was observed at room temperature (figure 3). The result is clear and confirms that change of the composite magnetoresistivity is proportional to the magnetization process and hence is really governed by the applied magnetic field.

Magnetoresistivity of the cermets at 300 and 77 K is shown in figure 4. Change of the composite magnetoresistivity with the temperature mainly depends on the metal phase concentration (figure 5). In the regime of metallic conductivity the GMR of the composite decreases more than two times after temperature reduction down to 77 K. The opposite behaviour was observed in the region with non-metallic conductivity (with larger content of SiO_n). GMR values increase in all these samples when the temperature goes down. The maximum value of GMR at 77 K (7%) was reached in the composite with maximum content of SiO_n, i.e. in the $(Co_{41}Fe_{39}B_{20})_{30}(SiO_n)_{70}$.

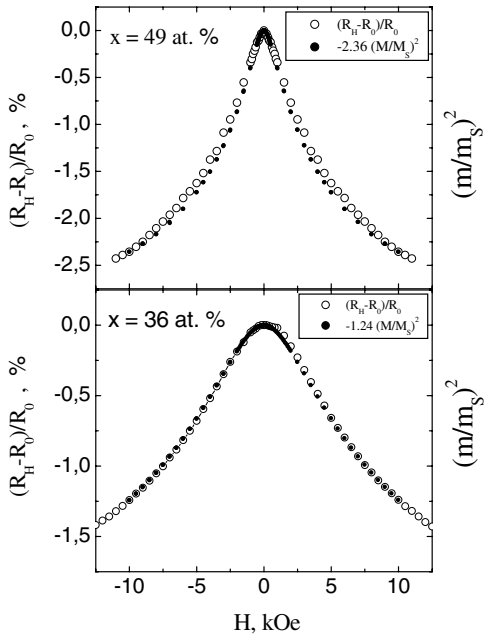

Figure 3. Field dependence of the magnetoresistivity (○) and square of the reduced magnetization (●) of the $(Co_{41}Fe_{39}B_{20})_x(SiO_n)_{100-x}$ composites. The M_S value was determined at 11 kOe. Concentration of the metal phase is shown in the figures.

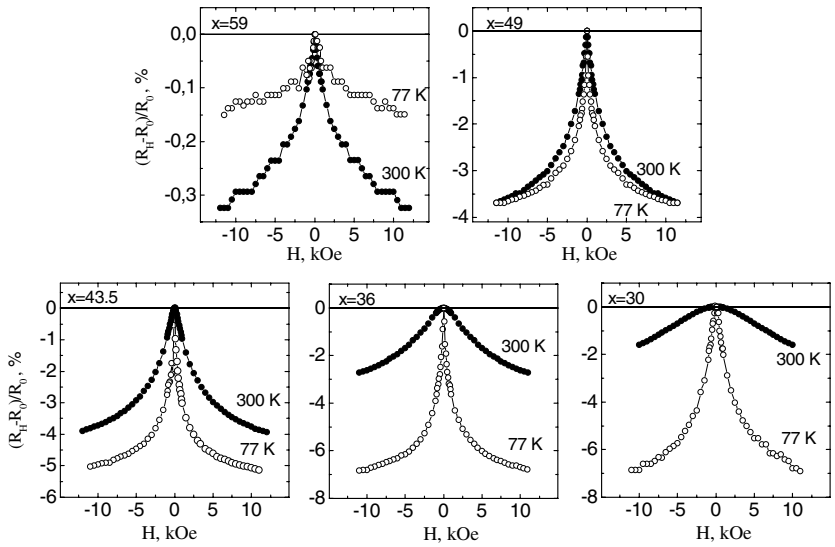

Figure 4. Change of the $(Co_{41}Fe_{39}B_{20})_x(SiO_2)_{100-x}$ composite's magnetoresistivity at 300 and 77 K. Concentration of the metal phase (x in at.%) is shown in the figures.

Keeping in mind the presence of the interrelationship between GMR and magnetization (figure 3), one should be interested in changes of the composite magnetization with temperature reduction. The magnetization curves of the $(Co_{41}Fe_{39}B_{20})_x(SiO_n)_{100-x}$ composites measured at 300 and 77 K are presented in figure 6. The $(Co_{41}Fe_{39}B_{20})_{59}(SiO_n)_{41}$ composite shows

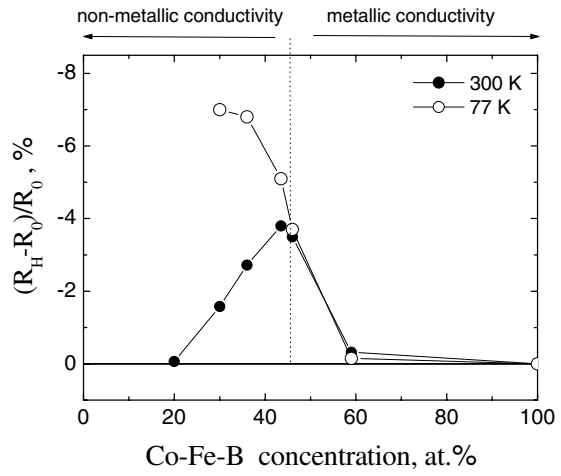

Figure 5. Magnetoresistivity of the $(Co_{41}Fe_{39}B_{20})_x(SiO_2)_{100-x}$ composites at 300 and 77 K against the $Co_{41}Fe_{39}B_{20}$ concentration.

ferromagnetic behaviour at both temperatures. It is clear that ferromagnetic properties of this composite arise because it is above the percolation threshold and a large part of the granules are joined into conducting and therefore ferromagnetic clusters. The presence of these clusters was confirmed by the temperature dependence of the composite's resistivity, which was similar to the dependence of simple amorphous alloys [10]. The thickness of the dielectric barriers separating granules and clusters is also very short in the composite and an exchange interaction can be present between these separated metal particles. In spite of thermal energy (kT), the exchange interaction orientates magnetic moments in parallel and leads to large domain formation, as happened in homogeneous alloys. That is also the reason why the GMR value is so small in this composite (figure 4). The cooling of the composite reduces the disordered effect of kT on the granule (or cluster) magnetic moments and increases the magnetization of the composite in a low field (figure 6). Therefore, even without a magnetic field the number of neighbouring granules (or clusters) with non-collinear magnetic moments becomes smaller at low temperature. Consequently, under the same applied magnetic field the number of tunnel 'barriers', joining metal granules (or clusters) with the moments oriented non-parallel, is smaller at low temperature compared to the number at high temperature. One should note that the tunnelling probability only through these 'barriers' (between non-collinear magnetic moments) can be changed by the applied field. In other words, a lower resistance in the composite regions can be changed by application of the field at low temperature. This is an explanation of the GMR reduction at cooling of the $(Co_{41}Fe_{39}B_{20})_{59}(SiO_n)_{41}$ composite.

The composites with larger SiO_n concentration are in a superparamagnetic state and no transition into some other magnetic state was observed in the samples cooled down to 77 K. The granule magnetic moments are disordered without the field in the superparamagnetic state but they begin to range along the field direction, if the field is applied. Increasing the magnetization of these composites on temperature reduction is due to a decrease of the value of thermal energy, which disorderly affects the magnetic moments. There is no magnetic hysteresis in the cermets at 77 K, so one can hardly suppose the presence of a magnetic interaction between neighbouring granules in this case.

At first glance, there is no correlation between the change of the GMR ($GMR_{77} - GMR_{300}$) and the magnetization ($m_{77} - m_{300}$) during cooling, as one could expect according to

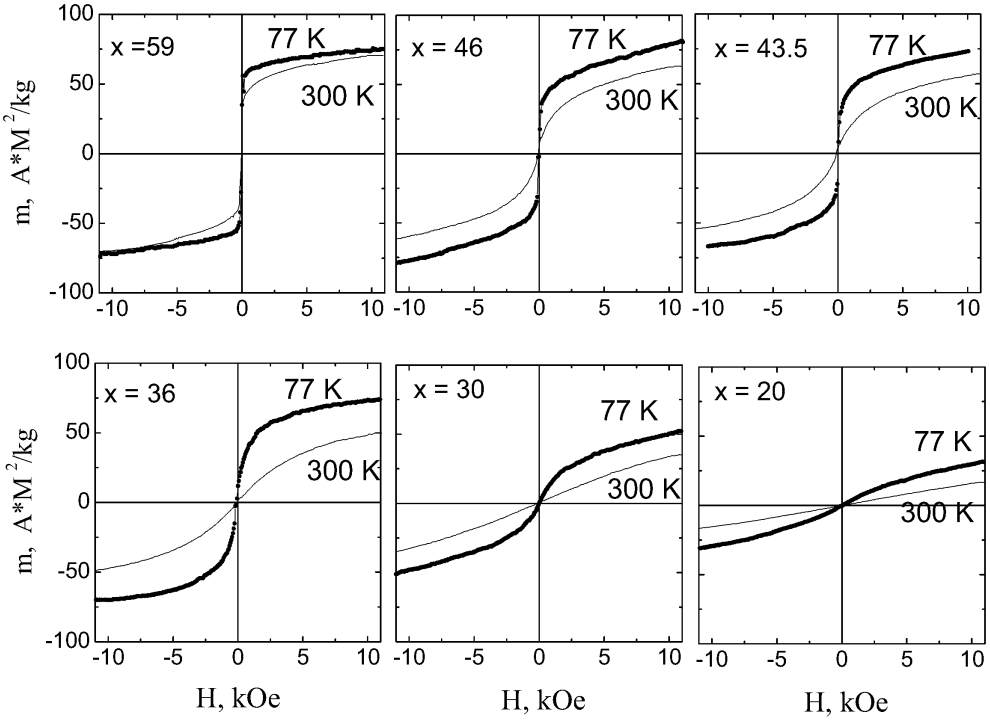

Figure 6. Magnetization curves of the $(Co_{41}Fe_{39}B_{20})_x(SiO_2)_{100-x}$ composites at 300 K (——) and 77 K (—). Concentration of the metal phase (x in at.%) is shown in the figures.

proportionality (see figure 3). This is not strange because one should not take into account the absolute value of the magnetization change or the square of this value. Actually, it is not very important how large or small magnetization varies after temperature reduction. Much more important is the relative change of magnetization compared to the magnetization value at 300 K ($[m_{77} - m_{300}]/m_{300}$). It is important because the relative change of magnetization determines how large is the change of the average angle between granule magnetic moments. If the relative change of magnetization is small it means that the moment's orientation as well as the condition for tunnelling does not vary too much. Hence, in such a case the GMR cannot be changed considerably and vice versa.

Unequivocal confirmation of the above statement had been found when the relative change of the magnetization was weighed with the reduced change of the GMR (figure 7). These results allow us to come to the conclusion that the observed increase of the GMR values after temperature reduction to 77 K is caused by the change of the average angle between the granule magnetic moments.

The $(Co_{41}Fe_{39}B_{20})_{36}(SiO_n)_{64}$ composite with large increase of the GMR value at cooling (figure 5) was chosen to study the GMR behaviour over a wider temperature range (2–300 K). Figure 8 presents the results obtained. The monotonic increase of the GMR values was observed under temperature reduction from 300 K to approximately 80 K, but after that, under the following temperature decrease, the magnetoresistivity dropped and reached ∼0.6% (one order less) at 2 K. Therefore, a clear maximum of the temperature dependence of the GMR in $(Co_{41}Fe_{39}B_{20})_{36}(SiO_n)_{64}$ composite was observed.

This result contradicts the published data obtained for Co–Al–O and Fe–Al–O cermets by the Fujimori group [4, 17] where magnetoresistivity monotonically increases with temperature

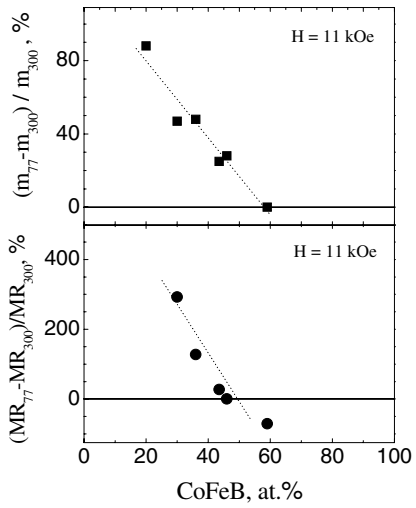

Figure 7. Concentration dependence of the relative change of the composite's magnetization and magnetoresistivity after cooling down from 300 to 77 K.

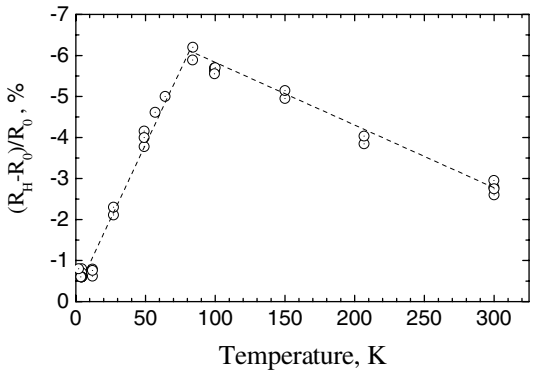

Figure 8. Temperature dependence of the GMR in $(Co_{41}Fe_{39}B_{20})_{36}(SiO_2)_{64}$ amorphous granular composite. The difference of the composite's resistance $(R_H - R_0)$ was determined at $H = 11$ kOe.

reduction. On the other hand, results that are similar to our data (maximum of the GMR in the average temperature range 80–200 K) were obtained in Ni–SiO_2 [6], Co–SiO_2 [13] and Fe–SiO_2 [18] cermets. Each group of results had its own explanation.

The monotonic increase of the GMR values, and especially the anomalously large increase of MR at low temperatures in Co–Al–O and Fe–Al–O cermets, is explained as a result of a spin-dependent higher-order tunnelling [19]. The Coulomb blockade suppresses the ordinary tunnelling of the electrons when temperature is being appreciably reduced. In such a condition, the higher-order simultaneous co-tunnelling of electrons between large granules through intervening small ones determines the electrical conductance as well as the magnetoresistivity itself of the cermets. It was shown that GMR is directly related to the order of the tunnelling process, i.e. the number of small granules involved in co-tunnelling when an electron is transferred from one large granule to another one with low charging energy. The definition of 'small' means that the charging energy of a certain granule is larger than the thermal energy.

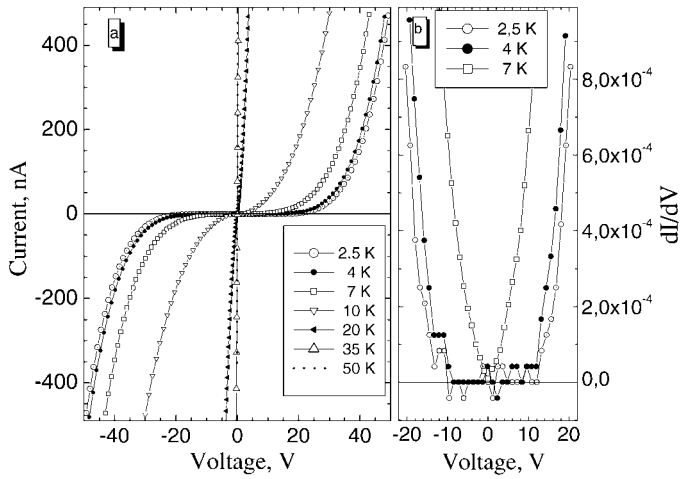

Figure 9. The voltage–current characteristics at different temperatures (a) and the derivative of the current with respect to voltage (b) for $(Co_{41}Fe_{39}B_{20})_{36}(SiO_2)_{64}$ composite.

Therefore this granule can take part in the co-tunnelling processes only as an intermediate element. The temperature reduction leads to the situation when the number of large granules that can be charged by the thermally activated electrons decreases and the tunnelling order increases accordingly.

The tunnelling conductivity is mainly responsible for the charge transfer in the studied $(Co_{41}Fe_{39}B_{20})_x(SiO_n)_{100-x}$ composites [20]. Therefore, it is no surprise that a very strong Coulomb blockade was observed in the $(Co_{41}Fe_{39}B_{20})_{36}(SiO_n)_{64}$ composite. The voltage–current characteristics of the $(Co_{41}Fe_{39}B_{20})_{36}(SiO_n)_{64}$ composite measured at different temperatures are shown in figure 9(a). The curves are extremely non-linear, especially at lower temperatures. Moreover, the derivative of the current with respect to voltage shows that current does not flow through the sample at the lowest temperature in spite of a high bias voltage, even at 10 V (figure 9(b)). A small temperature increase (several degrees) leads to the appearance of the non-zero electrical conductivity. We believe that a regime of full Coulomb blockade, when electrons are not able to leave a granule because their energy is less than the charge energy, is realized at the lowest temperature. Therefore, depending on the temperature, different conductivity modes can be reached in the composites: full blockade, partial blockade (this is supposed to be the optimal case for the maximum GMR according to [19]) and so on. Nevertheless, GMR of the studied composite decreases with temperature reduction from 80 to 2 K. Hence, Coulomb blockade does not provide enhancement of the GMR in our case.

According to another point of view [6, 13], the maximum of the temperature dependence of the MR is related to the change of the cermet's magnetic state. It was pointed out [6, 13] that granular composites, containing ferromagnetic metal granules, show superparamagnetic behaviour at room temperature but ferromagnetic ordering of the granule moments arises in cermets on temperature reduction. Within the framework of the proposed model, the GMR is largest at the superparamagnetic–ferromagnetic transition temperature. This explanation creates some doubts. The existence of strong exchange interaction between nano-granules, separated by a non-magnetic barrier of 1–3 nm, is hardly possible. As was estimated [21], exchange interaction between isolated granules is very weak and does not lead to any magnetic

ordering of the moments. On the other hand, dipole–dipole interaction (stronger than the exchange interaction) was observed in granular composites [21, 22], and some sort of magnetic ordering was formed in the composites. Therefore, one can suppose that ordering of the magnetic moments on decreasing temperature happened in the composites due to dipole–dipole interactions. Formation of such a correlated system of magnetic moments leads to a reduction in magnetoresistivity. Nevertheless, to be sure of the origin of the GMR maximum a precise magnetic investigation at low temperatures has to be done.

4. Conclusion

GMR as well as magnetization processes were studied at different temperatures in amorphous granular composites $(Co_{41}Fe_{39}B_{20})_x(SiO_n)_{100-x}$ for a wide concentration range ($20 \leqslant x$, at.% $\leqslant 59$). At room temperature the field dependence of the composite's magnetoresistivity coincides with the field dependence of the square of the reduced magnetization. The GMR enhancement in the composites with large dielectric content (below the percolation threshold) after cooling down to 77 K was observed. It has been shown that the magnetoresistivity enhancement directly correlates with the rise of the relative change in the composite's magnetization. It is supposed that the magnetoresistivity increase is due to a reduction of the average angle between the granule's magnetic moment because of a decrease in the disordering influence of thermal energy.

A relatively sharp and large decrease of the GMR in $(Co_{41}Fe_{39}B_{20})_{36}(SiO_n)_{64}$ composite (approximately one order in magnitude) was observed on a temperature reduction from $\sim$77 to 2 K. The temperature dependence of the magnetoresistivity exhibits thereby a maximum in the vicinity of 77 K. At the same time, a strong Coulomb blockade takes place in this composite at low temperature. Therefore, the Coulomb blockade in our case does not lead to enhancement of the magnetoresistivity at low temperature as was observed in other composites with different metal phases. A precise magnetic investigation has to be done to determine the nature of the GMR maximum.

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