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Spin-dependent transport in compacted powders of chromic dioxide CrO_2 with anisotropy of nanoparticle shapes

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Resistive and magnetoresistive properties of compacted powders consisting of nanosized particles of chromic dioxide CrO_2 with dielectric β-CrOOH shells are studied. Anisotropy of tunnel magnetoresistance which is responsible for by the magnetic field orientation relative to the specimen plane is observed. It is shown that the main contribution to the anisotropy of tunnel magnetoresistance is made by formation of the magnetic texture under powder pressing.
Keywords: half-metal, chromic dioxide CrO_2, nanosized particles, tuneneling magnetoresistance, resistive properties.

Исследованы резистивные и магниторезистивные свойства прессованных порошков, состоящих из наноразмерных частиц диоксида хрома CrO_2, покрытых диэлектрическими оболочками β-CrOOH. Обнаружена анизотропия туннельного магнитосопротивления, связанная с ориентацией магнитного поля относительно плоскости образца. Показано, что основной вклад в анизотропию туннельного магнитосопротивления возникает за счет формирования магнитной текстуры при прессовании порошков.

Спін-залежний транспорт у пресованих порошках діоксиду хрому CrO_2 з анізотропією форми наночастинок. *Н.В.Далакова.*
Досліджено резистивні та магніторезистивні властивості пресованих порошків, що складаються з нанорозмірних частинок діоксиду хрому CrO_2, покритих діелектричними оболонками β-CrOOH. Виявлену анізотропію тунельного магнітоопору, пов'язану з орієнтацією магнітного поля відносно площини зразка. Показано, що основний внесок в анізотропію тунельного магнітоопору виникає за рахунок формування магнітної текстури при пресуванні порошків.

1. Introduction

One of the central problems of the modern nanotechnology is production of functional materials with given magnetoresistive characteristics. For example, ultradisperse powders with the effect of giant magnetoresistance (GMR) have extensive applications in the modern electronic and spintronic devices. Such systems are used in magnetic recording devices, read heads of hard disks, magnetic memory elements. The ultradisperse powders with the GMR effect may be considered as granular materials with nanosized particles of ferromagnetic metal separated by potential (tunnel) barriers. The tunnel barriers are formed in the process of the powders synthesis. They may present either a natural degraded surface of ferromagnetic granules (particles) or a thin dielectric coating on the particle surface produced by the special technology. The

Table. d — Thickness of dielectric shall, H_P — coercive force at T = 5 K, found from the MR measurements, M_{max} — the maximum magnetization of the sample at T = 5 K, A — anisotropy of MR in the field H = 0.32 T or 0.28 T.

Sample	Shapes of particles	Shell of particles	d, nm	H_P, T (T = 5 K)	M_{max}, emu/g (H = 5 T, T = 5 K)	A, % (H = 0.2 T, T = 5 K) $J \perp$ plane	A, % (H = 0.2 T, T = 4.3 K) $J \parallel$ plane
1	spherical	β-CrOOH	3.6	0.0169	88.8	~0.2	2.9
2	acicular	β-CrOOH	1.8	0.0195	91.2	~2.0	6.4
3	acicular	β-CrOOH	1.73	0.0220	93.6		15.7

magnetoresistance (MR) of such a granular material depends on tunnel barrier properties and on relative orientation of the magnetization vector in adjacent granules. The probability of electron tunneling and hence, a negative MR is maximum when the magnetic moments in the adjacent granules are oriented in parallel [1]. In scientific literature such tunneling is named as spin dependent and corresponding magnetoresistance is called as tunnel MR.

The demands for materials with the higher GMR effect require a comprehensive study into influence of the properties of the tunnel barrier between ferromagnets, including the properties of the ferromagnet-insulator interface (among them the role of structural disorder in the barrier) on the tunnel MR. This problem is one of the important and not adequately investigated problems of the tunnel ferromagnetic transitions [1, 2]. In this context we have explored the effect of type and thickness of dielectric shells and particle shape on the tunnel resistance and MR of compacted powders of chromic dioxide CrO_2 [3]. It is shown that an increase in thickness of dielectric coating of CrO_2 particles causes the tunnel MR increase but only up to a certain limit after which MR begins to decrease with increasing the interlayer thickness. It would appear natural that for rather thick intergranular dielectric interlayers the granulated samples transform into system of completely isolated granules where the tunneling and tunnel MR are not exist at all. Except the properties of the tunnel barrier, the value of MR may depend on particle shape and size, powder density and magnetic field direction. MR of the granulated compacted powders is isotropic. At the same time one can assume that at the micro-level there is anisotropy property which is determined by the geometric anisotropy of the particle shape. To check that assumption the paper concerns possible influence of the particle shape anisotropy on the MR effect of the compacted CrO_2 powders. We studied two types of the powders of chromic dioxide CrO_2, namely, the powders with almost spherical shape of particles and those with the needle ones. Chromic dioxide CrO_2 (fine-grained) has long been used in magnetic recording. This material is ferromagnetic half-metal [1, 4, 5] with $T_c \approx 390$ K. In half-metals the conduction band at the Fermi level has carriers of only one spin polarization. At rather low temperatures the value of polarization P in CrO_2 can approach 100 % [5]. Here $P = (N\uparrow - N\downarrow)/N\uparrow + N\downarrow)$, $N\uparrow$ and $N\downarrow$ are the densities of electron states with spin directed up and downward, respectively. Despite the fact that the intrinsic magnetoresistance of monocrystalline CrO_2 is about 1 % (for H = 1 T) at the room temperature [1], MR of the compacted CrO_2 powder with particles coated with a thin insulator layer, appears to be gigantic. Its value can reach substantial magnitude (30 % or more) at the low temperature and small fields [4, 6].

2. Experimental

The powders under consideration were prepared by the method of hydrothermal synthesis with special admixtures that controlled nucleation, growth, size and shape of particles. Then the powders were stabilized (a layer of orthorhombic chromium oxyhydroxide, β-CrOOH, being formed on the particle surface). General characteristics of the technology are given in Refs. 3 and 7. Once prepared the powders were thoroughly tested at the Department of Magnetochemistry of St. Peterburg State University. Lattice parameters obtained are a = 0.4419 nm and c = 0.2914 nm in rutile-like lattice that agrees well with the known data for pure CrO_2 [5]. Since oxyhydroxide β-CrOOH is formed on the surface of CrO_2 particles through topotactic transformation, the crystallographic distortions at the CrO_2 — β-CrOOH interface were insignificant. The dimensions of rectangular samples were 3×5×12 mm^3. The main characteristics of three investigated powders are given in Table.

Powder No.1 consisted of spherical CrO_2 particles coated with 3.6 nm thick shell of chromic oxyhydroxide β-CrOOH. The mean particle diameter was ≈120 nm. Powders Nos.2 and 3 consisted of needle particles of CrO_2 coated with β-CrOOH shell of different thickness. The mean length of the needle particles was ~302 nm and the mean diameter was ~22.9 nm. For the needle particles and the round ones the density of pellets was about 40 % and ~60 % of X-ray density of the material, respectively. More severe pressing is made if the particles have less distinct anisotropy of the shape. The needle particles of CrO_2 were monocrystalline formations consisting basically of two domains. The vector along the length of such a particle is almost coincident with the direction of tetragonal axis **c** which is simultaneously the axis of easy magnetization. On pressing the pellets, the needle particles are mainly oriented in the plane of pressing normal to the applied load. In that case the orientation of the particles in the plane is rather disordered. Thus, for the powders with needle particles there is assigned direction **x** which is parallel to the vector of the applied load or axis of compaction and where the mean distance between the particles is a minimal one. The component of the density tensor in this direction is supposed to be larger than that in the plane of pressing.

The resistive measurements of the CrO_2 samples were performed with use of standard four-point probe technique under conditions of given current (J = 100 μA) and fulfillment of the Ohm law. When measuring the temperature dependence of resistance, the current was passed along the maximum length of the sample within the plane of pressing. Separation between the potential contacts was 8 mm. Voltage and current were recorded with nanovoltmeter Keithley-2182 and multimeters Keithley-2000. The magnetic properties were measured with vibration (77 Hz) and SQUID (Quantum Design) magnetometers.

3. Results and discussion

The temperature dependences of resistivity for three samples of CrO_2 are shown in Fig. 1. The temperature dependence of resistivity for sample No. 1 was almost similar to the exponential one $\rho(T) \propto \exp(1/T)$ at $T < 20$ K. For the samples with needle CrO_2 particles (Nos. 2 and 3) the dependence $\rho(T)$ at $I \leq 50$ K agreed quite well with the Mott law of variable range hopping conduction for 3D systems: $\rho \approx \rho_0\exp(T_0/T)^{1/4}$. Thus, all the samples demonstrated a tunnel behavior of the low-temperature conduction. Among the three samples, No. 1 with thicker dielectric β-CrOOH shell (3.6 nm) had the higher resistivity, while sample No. 3 with the thinnest dielectric shell had the lowest resistivity. As the temperature was increased up to $T \approx 220$ K, that the sample demonstrated the minimal resistivity and then, with the further increase of temperature, it exhibited a transition to the metallic-type conductivity. The transition is supposed to be due to the higher temperature-induced formation of percolation channel consisting of metallic granules with weak inactivated tunneling barriers and/or metallic short-circuits.

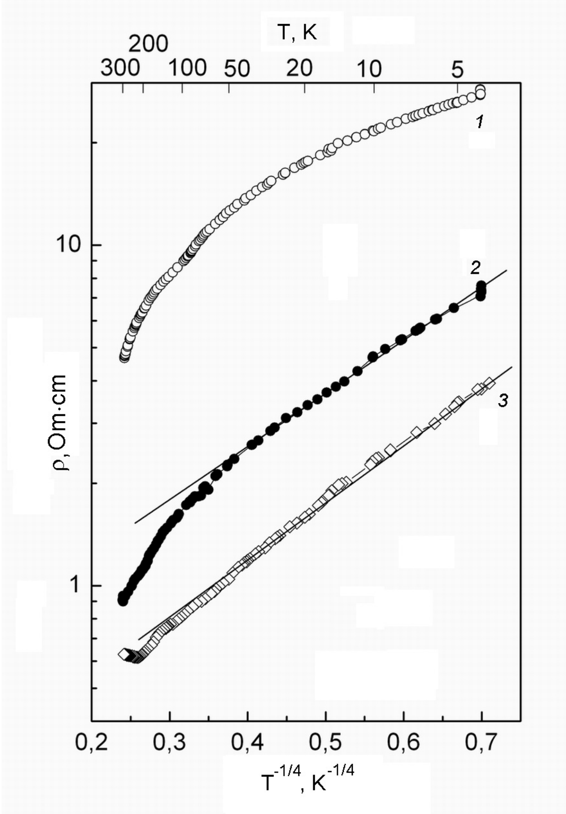

Fig. 1. Temperature dependences of resistivity for three powders of CrO_2. The number of the curves correspond to the samples numbers in Table.

The hysteresis curves of MR $\Delta R(H) = [R(H) - R(0)]$ were recorded by the normal

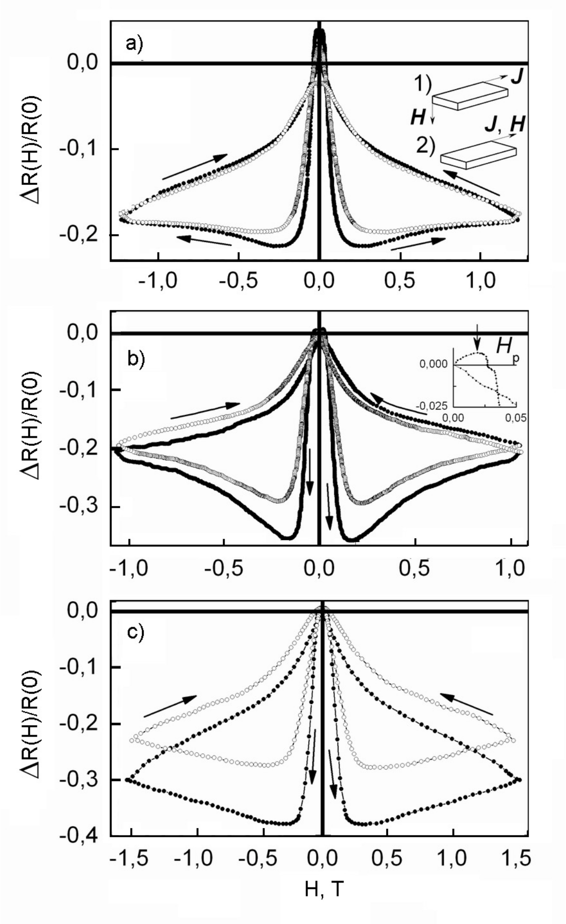

Fig. 2. Hysteresis curves of MR for compacted CrO_2 powders at T = 4.3 K: (a) – for powder No. 1 with rounded particles, (b) – for powder No. 2 with needle particles and (c) – for powder No. 3 with needle particles. Current and magnetic field directions are shown in Fig. 2a. The solid circles illustrate the magnetic field orientation in the sample plane (inset (2), $H\|J$) and the open ones correspond to H orientation normal to the sample plane (inset (1), $H\perp J$).

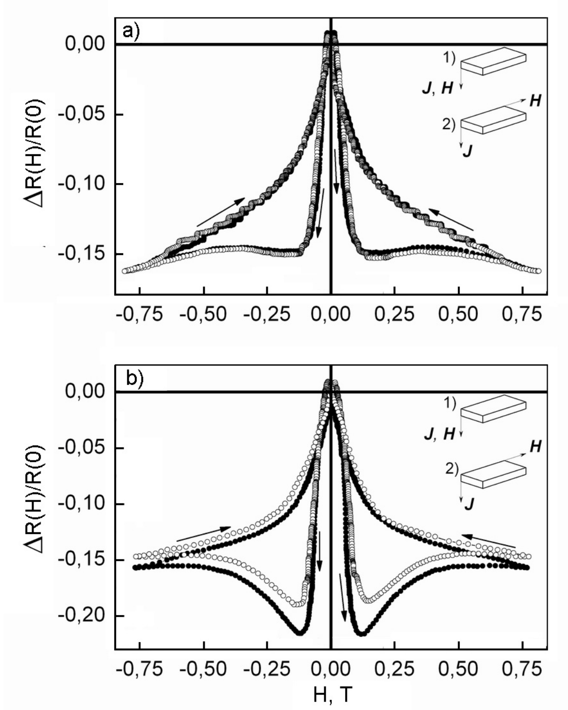

Fig. 3. Hysteresis curve of MR for compacted CrO_2 powders at T = 5.07 K: a is for powder No. 1 with rounded particles, b is for powder No. 2 with needle particles. The directions of current and magnetic field are shown in insets. The open circles correspond to H orientation which is normal to the sample plane and parallel to current (inset 1) and the solid ones correspond to H orientation in the sample plane perpendicularly to current (inset 2).

record protocol for hysteretic cycles of magnetization at different orientations of current and magnetic field (Figs. 2 and 3). The longitudinal magnetic field H_{II} was aligned within the sample plane while the transverse one $H_\perp$ was normal to the plane. The current and magnetic field orientations are shown in the insets of the corresponding Figures. The arrows indicate the field input and output directions. All the powders demonstrate two types of the hysteretic behavior of $\Delta R(H)/R(0)$. At the low fields one can observe the hysteretic behavior of the tunnel MR with two peaks of positive MR under typical fields H equal to $+H_p$ and $-H_p$, where H_p corresponds to coercive force H_c. The position of $+H_p$ is illustrated by the arrow in the inset (expanded scale) of Fig. 2b. The values of H_p for the three samples with the magnetic field and current orientations in the sample plane are listed in Table. As it seen from Table, the value of coercive field H_p is higher for the powders with needle particles. For the fields that are somewhat higher than H_p, one can observe an additional intersection of the curves $\Delta R(H)/R(0)$ during magnetic field input and output. Some possible reason of this second type of hysteresis is discussed in detail in Ref. 8 and it is associated with the percolation behavior of tunnel conductivity at the low temperatures. Each of the samples studied demonstrated the high tunnel MR at the low temperatures and small fields. In such cases one can observe the distinct magnetic anisotropy of MR associated with the field orientation in the sample plane. Thus the value of negative MR in the longitudinal field is higher than in the transverse one. This suggests that in the longitudinal field orientation the velocity of the sample magnetization

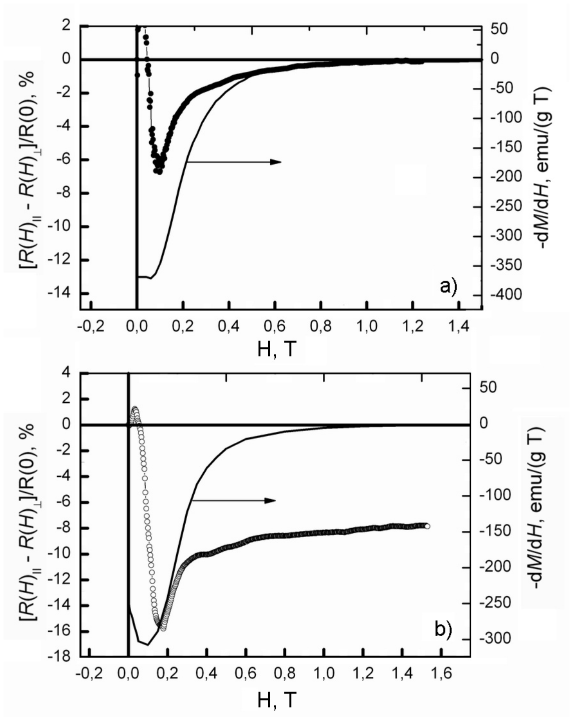

Fig. 4. Anisotropy $A = [R(H_{II}) - R\ (H_{\perp})/R(0)$ (the left ordinate axis) and derivative of magnetization with respect to field $dM(H)/dH$ (the right ordinate axis) as functions of H at $T = 4.3$ K: (a) – for powder 1, (b) – for powder No. 3. The values of anisotropy A are plotted by the data shown in Figs. 2a and 2c.

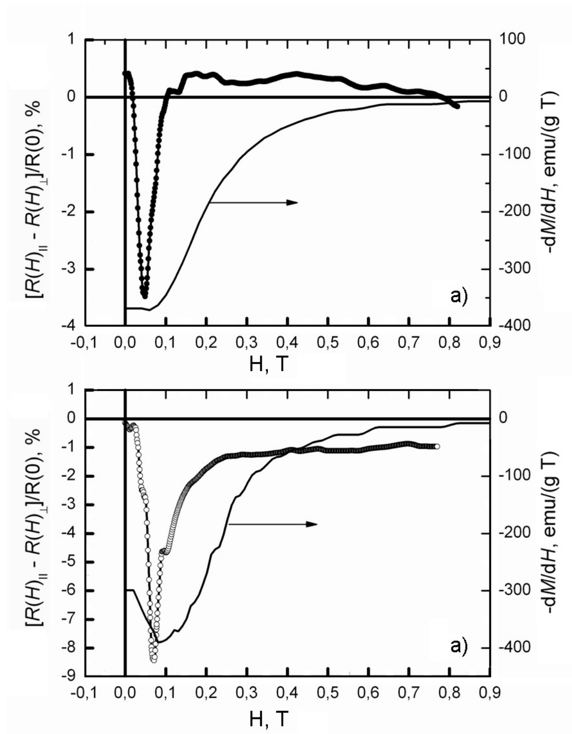

Fig. 5. Anisotropy $A = [R(H_{II}) - R\ (H_{\perp})/R(0)$ (the left ordinate axis) and derivative of magnetization with respect to field $dM(H)/dH$ (the right ordinate axis) as functions of H at $T = 5.07$ K: (a) – for powder 1, (b) – for powder No. 2. The values of anisotropy A are plotted by the data shown in Figs. 3a and 3b.

$dM(H)/dH$ is much higher. This effect is more pronounced in the powders with needle particles. Indeed, the anisotropy value calculated by the formula $A = [R(H_{II}) - R(H_{\perp})]/R(0)$ appeared to be several times larger for the powders with needle particles (samples Nos. 2 and 3).

Figures 4 and 5 show the field dependences on anisotropy $A(H)$ and magnetization derivative with respect to field $dM(H)/dH$ for two types of powders. The dependences $A(H)$ in Fig. 4 are plotted by the data shown in Fig. 2 and those in Fig. 5 — by the data in Fig. 3. It is clearly seen that the dependence $A(H)$ is non-monotonic and correlates with the behavior of $dM(H)/dH$. At the low fields ($H < 0.2$ T) the quick increase in magnetization $M(H)$ due to enhancement of spin polarization with field is followed by the increase in anisotropy $A(H)$. At the higher fields magnetization $M(H)$ increases much slowly, approaching saturation with increasing H ($dM(H)/dH \to 0$) and the enhancement of anisotropy $A(H)$ gives way to its decrease. In that case the dependence $A(H)$ becomes much weaker and tends to the constant value.

It should be emphasized that in the cases where the current is directed along the sample plane (Fig. 2), for the transverse orientation of magnetic field ($H_{\perp}$) there occurs a contribution to the total MR from the spin-orbit interaction. The value of this effect for massive ferromagnets is commonly of the order of 1 % [4]. For our samples anisotropy $A(H)$ is considerably large than one percent (see Table and Fig. 4). This suggests that there are some other sources of anisotropy in additional to the spin-orbit interaction. For the current normal to the sample plane (Fig. 3) there appears the negative contribution in conductivity from the spin-orbit interaction with longitudinal field orientation (H_{II}). Nevertheless, in this case, too, the inequality $|\Delta R(H_{II})| > |\Delta R(H_{\perp})|$ is fulfilled for needle particles (Fig. 3b). For spherical particles this inequality is fulfilled only at the low fields ($H \le 0.1$ T), as can be clearly seen in Fig. 5a. The fulfillment of the above inequality at the transversal current orientation suggests that there is a competitive contribution to the MR anisotropy.

Thus, the results obtained indicate that the negative MR is considerably larger in the case where the magnetic field is directed in the sample plane normally to the axis of compaction. Moreover, the most pronounced distinctions between $R_{II}(H)$ and $R_{\perp}(H)$ occur at low fields. It is suggested that because of the higher density of compacted powders in the direction of axis of compaction, the processes of magnetization and magnetization reversal in this direction may be difficult. It is for this reason that the total spin polarization along the axis of compaction was less than in the transverse direction. This results in a higher resistance and a lower negative MR both for the powders with needle particles and those with rounded ones. In the powders with needle CrO_2 particles it appears the additional contribution to the MR anisotropy due to the preferred orientation of these particles in the sample plane. The vector aligned with the particle length coincides with the direction of tetragonal axis **c** which is the easy magnetic axis of CrO_2. Hence it follows that in the powders with the needle particles the work done by the external magnetic field for the sample magnetization up to saturation is minimum while the spin polarization is maximum for the field align in the sample plane. This explains both the higher values of negative MR at the field orientation in the sample plane for the powders with geometrical anisotropy of the particle shape (powders Nos. 2 and 3) and the extraordinarily large values of the MR anisotropy for these powders as compared to the MR anisotropy of powder No. 1.

So, the above-mentioned experiments demonstrate that the compacted powders of CrO_2 have the magnetic anisotropy caused by the magnetic texture which is formed under pressing of the particles with shape anisotropy. The value of the MR anisotropy is dictated by the difference in velocity of the sample magnetization along the easy magnetic axis and normally to it. So, the value of the spin polarization and thus the value of the tunnel MR of compacted powders can be controlled both by the varying anisotropy of the particle shape and by the changing magnetic field direction with respect to the axis of compaction.

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