Short-range magnetic order in nanoceramic and bulk Mn3O4 irradiated electrons

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Abstract

The single-phase high-density nanoceramic Mn3O4 with the grain size 0.06 µm<d<0.5 µm is obtained by the method of the spherical-convergent shock waves. The influence of the particle size and radiation defects on the magnetic susceptibility χ(T) is investigated in the region of short-range magnetic order. It is shown, that the susceptibility in the nanoceramic is larger than in polycrystal, and the field dependences of magnetization have the nonlinear form. Electronic irradiation leads to a nonmonotonic change of the susceptibility depending on the fluence which is connected with the different type of radiation dis ordering.

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The increased interest in the nanocrystalline magnetic semiconductors is observed in recent years [1, 2]. The decrease of grain size to ~10 Å is the effective method of changing the properties of materials. In the ionic magnetic materials the size effect can be stronger than in the metallic compounds and can be realized even near Tc. Superexchange determining the magnetic order is short-range interaction and spreads only to the neighboring spheres. It depends on distances and angles of bonds between the magnetic ions. The principal effect of finite size on the magnetic properties of nanoparticle is breaking of the large number of exchange bonds for the surface spins because of the loss of 3D structural periodicity and oxygen vacancies in the surface layers. When some exchange bonds are broken there can be frustration of coupling and spin disorder. The decrease of grain size must lead to an increase in the number of intergrain boundaries and, accordingly, to an increase in the contribution of surface states. The size and form of particles, interaction between them have an effect on the formation of the magnetic properties of nanoparticles, therefore the magnetic properties of nanomaterials obtained by different methods can be different. The influence of the grain boundaries and interaction between the particles is manifested in the compacted materials most noticeable. In this work we report study on the influence of particle size and radiation defects on magnetic properties of Mn3O4. The method of action by the shock waves of high intensity for obtaining high-density ceramic Mn3O4

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was used. Earlier we investigated the influence of the nanoparticle size on the magnetic properties of low-dimensional antiferromagnet CuO, obtained by the indicated method [3]. The study the fine dispersed ceramics Mn$_3$O$_4$ can be useful for understanding of the magnetism of nanocrystalline manganites possessing large tunnel magnetoresistance. The presence of the second phase Mn$_3$O$_4$ is possible in the lanthanum manganites, therefore it is necessary to consider the contribution of this phase at the discussion of magnetic properties.

Fig. 1. Microstructure of Mn$_3$O$_4$: (a,b) – polycrystal; (c,d) – nanoceramic

After shock-wave action the density of ceramics Mn$_3$O$_4$ was considerably more (98%) than in initial polycrystals (80%). In this case fine dispersed structure is formed, the dislocation density and point defects rise considerably. The broadening of diffraction lines in comparison with the polycrystals indicates this. Form and sizes of crystallites were determined by means of the scanning electron microscope JEOL - 5500. In Fig.1 we represent the microstructure of the polycrystal and the nanoceramic Mn$_3$O$_4$. Particles size in polycrystals changes in the range 2 - 20 µm. In the nanoceramic the greatest quantity of small particles with the size 0.06 µm<d<0.5 µm was discovered in the center range of the sphere. Small particles had quasi-spherical shape; the larger particles had complex shape with the abrupt edges. Nanoparticles are grouped mainly near the boundaries of inside breakings. The clear dependence of change in grain size on radius of sphere is not observed in the loaded ceramics Mn$_3$O$_4$ in contrast to nanoceramics CuO [3].

Mn$_3$O$_4$ is ferrimagnetic material with the Curie temperature $T_c$=41.9K and complex magnetic structure [4]. In the spinel lattice ions Mn$^{2+}$ (S=5/2) occupy tetrapositions, and ions Mn$^{3+}$ (S=2) - octahedral sites. The canted-spin order of the Yafet-Kittel type realizes below $T$=33K, and spin-spiral structure along the axis [010] is observe in the range of 33K<$T$<39K. Above $T_c$ the temperature dependence of the reciprocal susceptibility $1/\chi(T)$ has hyperbolic shape typical for the ferrimagnets. The Curie-Weiss law with the effective magnetic moment, close to the theoretical value $\mu_{eff}=9.15\mu_B$ starts to be carried out only at $T$>400K [5]. Short-range magnetic order remains in the wide temperature range $T_c$<$T$<400K. This is confirmed by low value of $\mu_{eff}=6.85\mu_B$ obtained from the experimental curve which agrees with literature data. In the ferrimagnets the magnetic field recovers antiferromagnetic order near $T_c$ and it acts on each spin independently. Low value of $\mu_{eff}$ is explained by the fact that the part of magnetic moments is ordered antiferromagnetically in the field. That is why the "effective" number of isolated moments is lower than concentration of ions Mn.

In nanoceramic Mn$_3$O$_4$ the hyperbolic shape of dependence $1/\chi(T)$ remains at $T>T_c$, but values of susceptibility are larger. The temperature dependences of reciprocal susceptibility measured in differed fields for polycrystal and the nanoceramic are shown in Fig. 2. At a room temperature the susceptibility of the polycrystal almost does not depend on strength of the magnetic field (Fig. 3). In the nanoceramic the magnetic field affects $\chi$ value. The susceptibility decreases sharply with the increase of the field till $H$~4 kOe.
Fig. 2. Temperature dependences of the reciprocal susceptibility of Mn$_3$O$_4$: ◊ - polycrystal in $H=2.65$ kOe, o - nanoceramic ($H=2.65$ kOe), × - nanoceramic ($H=8.9$ kOe).

Fig. 3. The field dependences of magnetic susceptibility of the Mn$_3$O$_4$ at $T=300$ K: polycrystal - ◊ and nanoceramic - ×.

In the region of the short-range magnetic order 78K<$T<300$K the magnetization $\sigma=\chi H$ in the polycrystal is the linear function in $H$ with the extrapolation into zero. In the nanoceramics the magnetization can be represented in the form $\sigma=\sigma_0+\chi H$, where $\sigma_0$ is small value of spontaneous magnetic moment, which tends to decrease with temperature rise. High values of $\chi$ and nonlinear dependence $\sigma(H)$ point to the stronger spin correlations in the nanoceramic. An increase of the susceptibility in nanoceramic Mn$_3$O$_4$ can be connected with the number of factors. In the magnetic nanoparticles the loss of 3D periodicity, oxygen vacancies on the surface, the long-range elastic strains and increase in the surface anisotropy promote to the disordering of spins. The interactions between the particles attempt to preserve magnetic order. The competition of these factors influences on the magnetic properties of nanoceramic Mn$_3$O$_4$. The noncollinear ordering of surface spins can lead to an increase of $\chi$. For example, in antiferromagnetic compacted nanoceramic CuO the increase in the susceptibility is observed with the decrease of grain size $d<60$ nm [3]. In the oxides the tendency towards the reduction under action of the shock waves of high intensity is observed. Another reason for increase of $\chi$ in nanoceramic Mn$_3$O$_4$ can be an increase of the concentration of ions Mn$^{2+}$ as a result of the action of plastic deformations and high temperatures. In the oxides the tendency toward the restoration under action of shock waves of high intensity is observed. According to neutron diffraction studies in the nanoceramic Mn$_3$O$_4$ the oxygen content decreases to 3.96. For preservation of the electroneutrality some part of the cations reduces the valency and as a result total magnetic moment increases. The most probable reason for an increase of $\chi$ is displacement of $T_c$ to larger temperatures after shock-wave load. The increase of $T_c$ is connected with a decrease of lattice parameters and an increase in the exchange parameters. This promotes to local spin correlations and short-range magnetic order.

By the electronic irradiation the point defects are created not only on the particle surface, but also in their volume. A large quantity of defects frustrates exchange bonds and is able to lead to effects similar to the size effect. We compared the influence of electron radiation on the magnetic properties of polycrystal and nanoceramic Mn$_3$O$_4$. The temperature dependences of the reciprocal susceptibility of the polycrystal with the different fluences are shown Fig. 4. Nanoceramic has similar behavior of the susceptibility change from the dose in the region of short-range magnetic order (Fig. 5). At the small radiation dose $F=0.8*10^{18}$ cm$^{-2}$ the increase of susceptibility is observed both in the polycristal and in the nanoceramic. The dose growth $F\leq5*10^{18}$ cm$^{-2}$ leads to the decrease of $\chi$. This nonmonotonic behavior of susceptibility can be connected with different types of defects, which influence on the exchange bonds. At small radiation doses the light
ions of oxygen displace from their positions. In this case the distances between the magnetic ions remain, angles of Mn-O-Mn bonds change. The approach of the angles to 90° must intensify ferromagnetic exchange interaction between octahedral chains B-O-B. Another reason for an increase \( \chi \) is formation of spin polarons with the large magnetic moment near the vacancies. The heterogeneous magnetic state and the presence of the magnetic polarons in the temperature range \( T \geq 2T_c \) are typical for the magnetic semiconductors. With an increase of the fluence besides oxygen ions manganese ions also displace. Not only coupling angles change, but the distances Mn-O-Mn. It is possible to assume, that the increase in the distance between the magnetic ions leads to weakening of exchange bonds and decreasing of the magnetic susceptibility.

![Fig. 4. Temperature dependences of the reciprocal susceptibility of the polycrystal Mn₃O₄ with different fluences F: \( \times - 0; \Delta - 0,8*10^{18}\text{c}m^{-2}; \circ - 2,34*10^{18}\text{c}m^{-2}; \diamond - 5,0*10^{18}\text{c}m^{-2}. \)

Thus, in the region of 78K<T<300K the susceptibility of the loaded ceramic Mn₃O₄ is more than \( \chi \) values for the polycrystal. Basic reason for an increase of \( \chi \) is a decrease of lattice parameters accordingly and an increase in the exchange interactions. Irradiation by the small dose of electrons leads to strengthening of spin correlations. Decrease in the susceptibility is connected with the radiation disordering at the dose growth.

![Fig. 5. Temperature dependences of the reciprocal susceptibility of the nanoceramic Mn₃O₄ with different fluences F: \( \times - 0; \Delta - 0,8*10^{18}\text{c}m^{-2}; \circ - 2,34*10^{18}\text{c}m^{-2}. \)

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