Peculiarities of magnetic behavior of CuO nanoparticles produced by plasma-arc synthesis in a wide temperature range

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Abstract

Copper oxide nanoparticles, produced by direct plasmochemical synthesis in a low-pressure arc discharge plasma, show a wide variety of magnetic properties depending on the strength of the external magnetic field and the temperature. At low strength of the field and throughout the studied temperature range the ferromagnetic state dominates. This state is caused by disordering of the spins on the surface of the nanoparticles. At high strength of the field and under the temperatures of less than 200 K, nanoparticles exhibit a paramagnetic state due to the spin-glass behavior of copper atoms. At high strength of the field (more than 3 kOe) and under the temperature of above 300 K, the diamagnetic state of nanoparticles is observed, due to local eddy currents caused by oxygen vacancies. The temperature of antiferromagnetic ordering under study is significantly lowered (down to ~ 100 K).

Key words: CuO nanoparticles, vacuum arc, ferromagnetism, diamagnetism.

I. INTRODUCTION

During the studies of nanopowders, produced in a low-pressure arc discharge plasma, the significant influence of the cooling rate on the magnetic properties of the produced materials was revealed. Earlier, it was shown in [1, 2] that the introduction of nonsuperconducting nano-sized CuO powders, produced in low-pressure arc discharge plasma, into polycrystalline HTSC $YBa_2Cu_3O_{7-y}$ leads to the production of new types of composites with nano-sized defects in the form of droplets and whiskers. Studying the superconducting properties of the produced composites revealed a substantial increase in the density of critical current and the peak-effect in the range of strong magnetic fields. Thus, further study of the magnetic properties of the produced CuO nanopowders over a wide temperature range, is of current importance. To prevent the influence of magnetic impurities

and the phase inhomogeneity of CuO, there were undertaken the particular measures, described in detail in [3-7].

II. RESULTS AND ANALYSIS

Figure 1 shows the temperature dependences of the magnetic moment $M(T)$ of the produced sample of CuO nanopowder upon cooling in a field and without a field (ZFC and FC correspondingly) for various external magnetic fields.

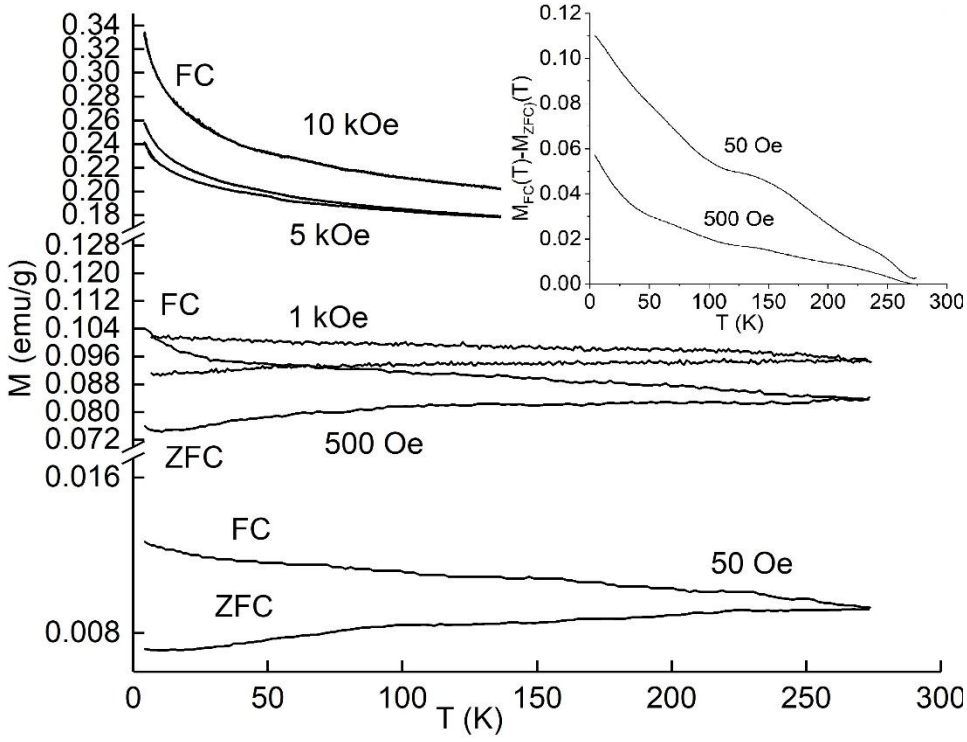

FIG. 1. Temperature dependences $M(T)$ of CuO nanoparticles in different external fields under the mentioned ZFC and FC conditions: 50 Oe, 500 Oe, 1 kOe, 5 kOe, 10 kOe. On the inset: the dependencies $M_{ZFC}(T) - M_{FC}(T)$ for the external fields of 50 Oe, 500 Oe.

In the weak fields, the divergence of the curves $M(T)$ under the conditions of ZFC and FC is significant, but with the increase of the field strength this discrepancy decreases substantially. Increase of the external field causes the significant change of the character of the curves $M(T)$.

This behavior of CuO nanoparticles fundamentally differs from the properties of the "bulk analogue", in particular polycrystalline CuO [8-13]. The curve $M(T)$ in the field of H = 1 kOe, also shown in Fig.1, has a characteristic feature. It is the independence of the magnetic

susceptibility (or M/H ratio) from the magnetic field. While the temperature is increased, a maximum is observed in the neighborhood of T_N, and then the temperature is decreased gradually in the range of 300-550 K [12]. We should also note, that the values of the magnetic susceptibility for CuO nanoparticles significantly exceed the value of the magnetic susceptibility of polycrystalline CuO (in the field of H = 1 kOe the exceeding is observed practically by an order of magnitude).

The described peculiarities of the magnetic behavior of CuO nanoparticles are also revealed in the character of the curves $M(H)$, as shown in Fig.2.

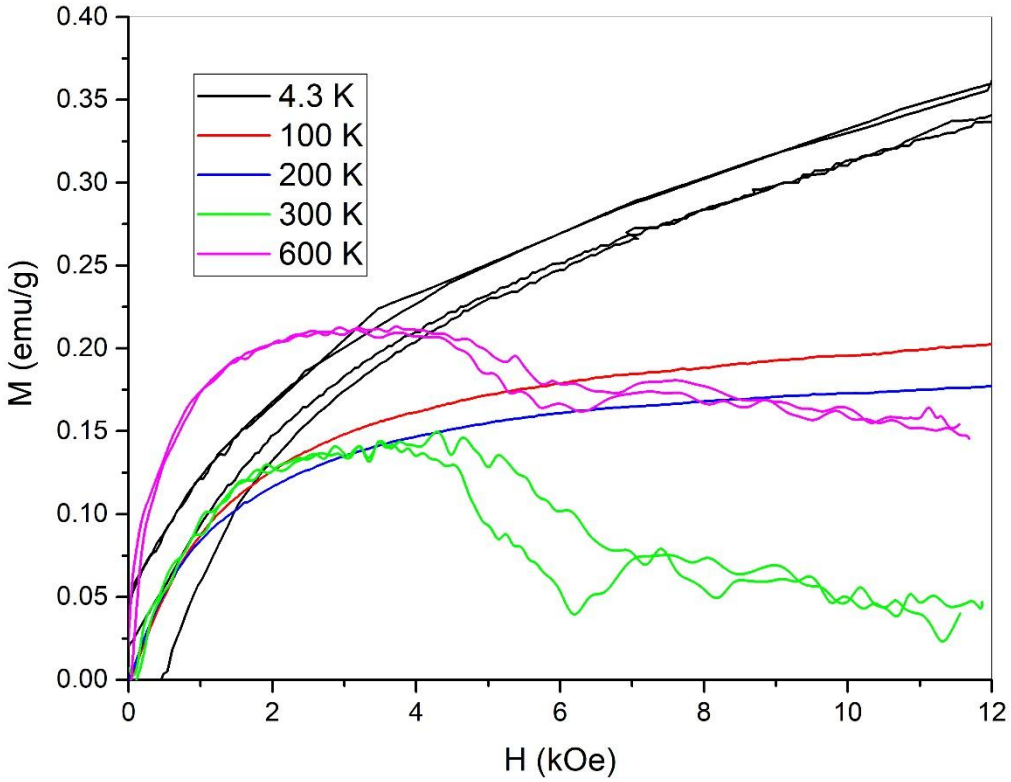

FIG. 2. The dependence $M(H)$ of CuO nanoparticles at the mentioned temperatures.

At T = 4.2 K, the $M(H)$ curve shows a hysteresis with a coercive force of about 0.5 kOe. The saturation is not reached even at the strength of the external magnetic fields of ~50 kOe. At temperatures of 100-200 K, the curves $M(H)$ of CuO nanoparticles also demonstrate ferromagnetism up to ~ 2 kOe with the subsequent transition to the paraprocess without achieving saturation. At the temperatures of 300 K and 600 K CuO nanoparticles exhibit unusual magnetic properties. First, the magnetic susceptibility of CuO nanoparticles in the region of up to 2 kOe sharply increases. CuO nanoparticles show the clear ferromagnetic behavior with the saturation magnetization (M_S) of 0.13 and 0.2 emu/g, respectively. Secondly, at 4 kOe the diamagnetic mechanism is activated, moreover the diamagnetic

moment substantially exceeds the ferromagnetic one. The curve $M(H)$ abruptly reaches the minimum at 6 kOe, and then steadily declines. Third, a diamagnetic hysteresis is observed. The value $M_{max}(H)$ for 300 K and 600 K is found to be 0.05 emu/g.

The observed behavior of the magnetic properties of CuO nanoparticles leads to the conclusion that the investigated system contains several magnetic phases, which reveal themselves at different temperatures and magnetic fields. The ferromagnetic (FM) phase exists throughout the investigated temperature range. The paramagnetic phase appears for the temperature from 4.2 K to 200 K, while the contribution to magnetization has a decreasing character. The investigated CuO nanoparticles do not show antiferromagnetic behavior in the vicinity of the point corresponding to 230 K. For the studied CuO nanoparticles a significant decrease in the Neel temperature is observed.

Taking into account the rather rapid decrease in the magnetic moment caused by the "paramagnetic" contribution with increasing temperature (Fig. 2), and the temperature dependences of magnetic moments in the constant field (Fig. 1), we can found an approximate estimation of FM contribution $M_{FM} \sim 0.2$ emu/g (for low temperatures). Taking into account that the effective value of the magnetic moment of Cu in CuO is equal to ≈ 0.7 μ_B (where μ_B is the Bohr magneton) [15], we can conclude that the fraction of FM-ordered atoms is found to be $\sim 4\times10^{-3}$ of all the copper atoms. Moreover, in this case the magnetic moments of the FM phase are in a locked state.

The authors of [10] explain this phenomenon by disordering of spins (deviation from collinearity) mainly on the surface of the nanoparticles, which leads to the appearance of a spontaneous magnetic moment. Noncollinearity of spins is a reason of the increase of susceptibility in high magnetic fields with a decrease of the nanoparticle size, which is due to the appearance of an additional paramagnetic or ferromagnetic contribution [14] and the weakening of the exchange interaction between the sublattices. The value of the spontaneous magnetic moment depends on the type of defects and can be estimated from the formula: $\mu_{FM} \sim N^b\times\mu$, where N is a number of magnetically active atoms in a particle, μ is a magnetic moment of this atom, and the exponent of b is 1/3, 1/2 and 2/3 for the cases of defects on the surface, in the volume of a particle, and for an odd number of ferromagnetic planes. According to [3-7], CuO particles have an average size of ~ 10 nm and contains about $75^3 \sim 4.2\times10^5$ of Cu^{2+} atoms. For the obtained above value of the fraction of FM-ordered moments of copper atoms ($\sim 4\times10^{-3}$), the estimated number of FM-ordered atoms is found to be $\sim 1.7\times10^3$, which is close to the investigation of [15], where the cause of the FM-moments existence is found to be an odd number of FM planes: $N^{2/3} \sim 5.6\times10^3$ for $N \approx 4.2\times10^5$.

It is known [9, 16] that in CuO the exchange interaction is of the order of ~ 400 K, and the short-range ferromagnetic order can be remained up to high temperatures.

The character of the dependence of the magnetic moment for the paramagnetic contribution on the temperature, in fields of H = 5 and 10 kOe (Fig. 1), indicates a "paraprocess", which, in the case of noninteracting spins, can be described by the Brillouin function B (H, T). However, for the low-temperature region the dependences M(T) in the fields of H = 5 and 10 kOe vary with the temperature more slowly than the Brillouin function with the magnetic moment of ≈ 0.7 μ_B. This fact and the observed discrepancy of the M(T) dependences in the fields of H = 5 and 10 kOe for the FC and ZFC conditions indicate the spin-glass behavior of the part of the spins in this subsystem. The calculation of the dependence M(H) at T = 4.2 K with only two terms without taking into account the hysteresis of $M_{FM}(H)$ ~ const ~ 0.2 emu/g and $M_{PM}\times B(H)$ gives the value of the "paramagnetic" contribution M_{PM} ~ 1 emu/g (±20 %). This value corresponds to ~ 2% of the total number of copper atoms, which show the surface atoms by order of magnitude. Thus, we can consider the spin-glass subsystem of surface atoms that exhibit paramagnetic properties at low temperature and high magnetic fields.

The estimation of the Neel temperature for the investigated system of CuO nanoparticles is a rather difficult task, since the paramagnetic contribution dominates in the low-temperature region. The dependences M(T), measured under the ZFC conditions in weak fields of 50 and 500 Oe, in which the contribution of the paramagnetic phase is insignificant, show the greatest increase in the temperature range up to 100 K, so it can be assumed that the Neel temperature for the studied CuO nanoparticles is of the order of about 100 K, which is significantly lower than for the "bulk analog". This is confirmed by a sharp increase (with decreasing temperature) of the difference $M_{ZFC}(T) - M_{FC}(T)$ (inset in Fig. 1) in the temperature range below 100 K. A similar effect was observed by the authors of [6] in the vicinity of the point corresponding to the Neel temperature T_N. Despite the fact that the difference $M_{ZFC}(T) - M_{FC}(T)$ is not a strict proof of the transition to the AF state, nevertheless, the surface spins can be exchange-coupled to the AF "core".

At the high temperature (above the Neel temperature) and in the magnetic field (of ~ 3 kOe), one more phase (diamagnetic) reveals itself and begins to dominate over all the other magnetic phases. The reason for the appearance of diamagnetism is not connected with the disordering of the spins and with the presence of other crystalline phases besides the monoclinic crystal system of tenorite. The most probable reason for the appearance of a high diamagnetic moment is the local eddy currents caused by oxygen vacancies. Only the

appearance of oxygen vacancies and, consequently, the presence of excess charge carriers can lead to essentially different fundamental feature, particularly, the phase separation of the system and the appearance of diamagnetic states in the antiferromagnetic (AF) matrix. To confirm this hypothesis, XPS spectra were studied (Fig. 3). The direct determination of the chemical and electronic state of oxygen and copper on the surface of CuO nanoparticles was carried out along the lines Cu2p, O1s. The figure also shows the results of adjustment by the Gaussian and Lorentz functions.

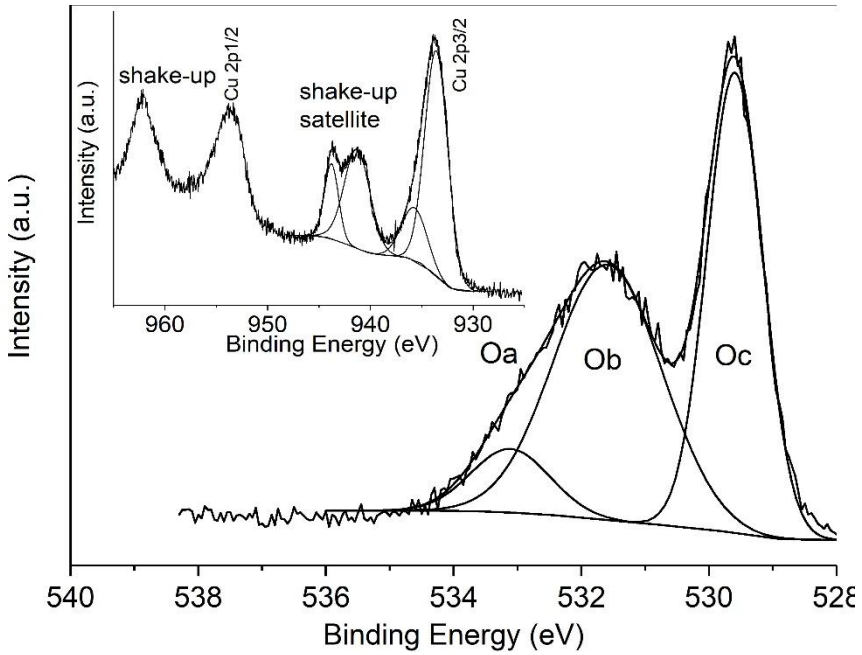

FIG. 3. Spectrum of XPS O 1s of the level of CuO nanoparticles at 300 K. The inset shows XPS Cu 2p spectrum of the level of CuO nanoparticles at 300 K

Copper oxide CuO is formed on the surface of the nanoparticles. It is characterized by practically one copper state (doublet Cu2p 3/2-1/2 with a splitting of 19.9 eV, E_b (Cu2p 3/2) = 933.3 eV). The spectrum Cu2p contains a "shake-up" satellite, which is characteristic for the state of Cu^{2+}, it is located at ~9 eV from the main peak.

The O1s spectrum contains the main Oc component, corresponding to oxygen in the CuO oxide, characterized by the binding energy E_b (O1s) = 529.3 eV, and also the second Ob component is observed in the form of the well-developed shoulder with a binding energy of E_b (O1s) = 531.2 eV. It was previously reported that this peak can develop with increasing oxygen loss and can be associated with O_2 ions in oxygen-deficient regions. Thus, the Ob

component can be associated with the concentration of oxygen vacancies. The relative content of this component was found to be 46%.

The peculiarity of the morphology of the investigated nanoparticles is that, due to the high cooling rate, the surface of the nanoparticles consists of particles of ~ 2 nm in size, which, depending on technological factors, can be arranged in complex structures. Probably, the conduction currents exist as vortices in these particles, creating a diamagnetic response at high temperatures and magnetic field strengths. The mechanism of interaction of the magnetic moments created by these currents is of special interest.

III. CONCLUSION

Thus, the analysis of magnetic data leads to the following model of the magnetic state of CuO nanoparticles produced in the low-pressure arc discharge plasma. The "core" of particles has the antiferromagnetic order with the Neel temperature which is much less than the temperature of the bulk analog ~ 100 K. The surface copper atoms, depending on the strength of the external magnetic field and the temperature, reveal themselves as a "paramagnetic", or more precisely, partially spin-glass subsystem. They can be exchange-related both to the "core" of the particle, and to the ferromagnetic component, which caused by the short-range ferromagnetic order existing over a wide range of temperatures. The oxygen vacancies determined the presence of the excess charge carriers and lead to phase separation of the system and the appearance of diamagnetic states in the antiferromagnetic (AF) matrix.

Acknowledgements. This study was supported by the Russian Science Foundation. (Project No 16-19-10054).

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