# GIANT MAGNETORESISTANCE IN DIFFERENT MAGNETIC STATES OF FERROMAGNETIC NANOPARTICLE SYSTEMS

S.M. KONOPLYUK, V.V. KOKORIN, YU.S. LEVCHUK, L.E. KOZLOVA

Institute of Magnetism, Nat. Acad. Sci. of Ukraine
*(36b, Academician Vernadsky Blvd. Kyiv 03142, Ukraine; e-mail: ksm@im.imag.kiev.ua)*

UDC 537.633.9; 537.622


The decomposed solid solutions of Cu–Ni–Fe and Cu–Mn–Al alloy systems have been investigated in order to determine the magnetoresistance in different magnetic states formed in a system of magnetic nanosized particles. Three collective magnetic states, namely, superparamagnetic, superferromagnetic, and superspin glass ones have been identified by magnetic susceptibility measurements. The temperature and field dependences of the magnetoresistance demonstrate peculiarities related to each magnetic state.

## 1. Introduction

Magnetoresistance is a subject of extensive studies due to the high practical importance of applications related to storing and reading the information, design of magnetosensitive elements, etc. In particular, GMR (giant magnetoresistance) observed in multilayer films [1, 2] and granular structures [3, 4] originates from spin-dependent electron scattering and represents a drop of resistance under an applied magnetic field. In the layered structures such as sandwiched spin valves, multilayers with antiferromagnetic interlayer coupling, and ferromagnetic multilayers with different coercivities, GMR depends on the relative orientation of the magnetic moments of layers [5]. In granular materials which are often ones with dispersed magnetically ordered nanoparticles in a nonmagnetic (paramagnetic or diamagnetic) matrix, GMR depends on the collective behavior of the magnetic moments of granules (particles), and its value is governed by the intergranular distance, magnetic moment, and size of granules. The granular structures can be formed in the film and bulk states. In the latter case, the magnetic nanoparticles can be obtained by a precipitation as a result of the decomposition of supersaturated solid solutions. They are observed in many metallic systems consisting of immiscible components, e.g. Cu–Ni–Co, Cu–Co, Ni–Mn, Cu–Ni–Fe, Cu–Mn–Al, etc. The GMR of bulk materials is less practically applicable than that of films, and, therefore, less studied.

In the case of Cu–Ni–Fe [6] and Cu–Mn–Al [7] systems, there is a range of compositions, i.e. a miscibility gap, wherein a thermal treatment gives rise to dispersed ferromagnetic inclusions embedded in a nonmagnetic matrix. In this range, Cu–Mn–Al alloys decompose into the $Cu_2MnAl$ ($L2_1$) phase, which precipitates as nanoparticles and into the $Cu_3Al$ ($DO_3$) matrix phase. In the Cu–Ni–Fe system, a similar segregation occurs between Cu-depleted particles and the Cu-rich matrix. As shown in [8, 9], different magnetic states can exist in a system of the magnetic moments formed by inclusions dispersed in a nonmagnetic matrix. Under the condition $Kv_0 \ll k_BT$, where $K$ is the anisotropy constant, $v_0$ is the average volume of a single particle, and $k_B$ is the Boltzmann's constant, these states strongly correlate with the volume fraction of particles. For the Cu–Ni–Fe system, provided that the volume fraction $p = Nv_0$, where $N$ is the number of particles per unit volume, is less than 0.13–0.15, the magnetic moments of particles interact weakly, and the high-temperature state is superparamagnetic [9]. Thereafter, as the temperature decreases, the superparamagnetic phase is changed to a superspin glass one. If $p$ is more than 0.15, instead of the superspin glass state [9–12], at low temperatures, the superparamagnetic state transforms into a superferromagnetic one [10, 12, 13] which is characterized by the aligning of particle magnetic moments in one direction. Since GMR in granular solids depends, among other things, on the surface-to-volume ratio of particles [3], it is of interest to clarify the behavior of the magnetoresistance for different magnetic states by the example of bulk Cu–Ni–Fe and Cu–Mn–Al alloys with almost the same particle size. Based on the data obtained earlier [8, 9], two alloys with nominal compositions of Cu–22Ni–15Fe and Cu–9Mn–14Al have been explored.

## 2. Experimental

Ingots of Cu–Ni–Fe and Cu–Mn–Al were produced by the induction method in the Ar atmosphere. Chemical analysis corroborated the closeness of the alloys compositions with nominal ones. Specimens were produced by the spark cutting from ingots and measured to be $1.5\times1.5\times11$ mm$^3$. After the quenching from 1323 K to obtain a non-equilibrium state, the specimens of Cu–Ni–Fe were annealed at 873 K for 5 min in the salt bath of NaCl (72 wt.%) – CaCl (28 wt.%). This treatment was carried out in order to stimulate the formation of new phase precipitates. A similar procedure was undertaken in relation to Cu–Al–Mn specimens. Their quenching was performed from 1273 K and was followed by the annealing at 473 K for 50 min in an oil bath. Low field ac magnetic susceptibility and resistivity were measured as functions of temperature in the range from 77 to 723 K. Magnetoresistance was determined by the four-terminal method in the presence of a magnetic field applied in parallel or normally to the current direction. The data are displayed as $\Delta R/R = (R(H) - (R0))/R(0)$, where $R(H)$ is a resistance in a field $H$, and $R(0)$ is a resistance in zero field. It should be noted that no methods to identify the structure of the alloys were used in this work since the size and the density of particles are predetermined fairly well by the composition, quenching, and aging of alloys [8, 14].

## 3. Results and Discussion

As noted previously, the system should be treated provided $Kv_0 \ll k_{\rm B}T$. This means that the temperature range under consideration is above some blocking temperature $T_b$, because, otherwise, the magnetic moment of a particle is blocked by the anisotropy field and the particle behaves itself as a ferromagnetic one regardless of the overall volume fraction. In order to find out if this condition is fulfilled for the samples under study, the estimation of the blocking temperature should be performed. It was obtained in [15] that, for an arbitrary observation time, the blocking temperature obeys the relation $T_b{=}Kv_0/k_{\rm B}|\ \ln f/f_0|$, where $f$ is the frequency of a magnetic field, and $f_0$ is some constant (approximately, it can be associated with the electron Larmor frequency in the field of anisotropy). According to measurements reported in [8, 9] for specimens of the above-mentioned compositions and treatments, the average diameter of particles was 60 Å for Cu–Mn–Al, and 50 Å for Cu–Ni–Fe. Substituting 1000 Hz in the expression as the frequency of a magnetic field, $5\times10^3$ and $10^3$ erg/cm$^3$as the magnetic anisotropy constants for Cu–Ni–Fe and Cu–Mn–Al, respectively, one can find that the estimated blocking temperatures are less than 1 K. As a result, we can conclude that the magnetic moments of particles cannot be blocked by the magnetic anisotropy field in the temperature range of measurements.

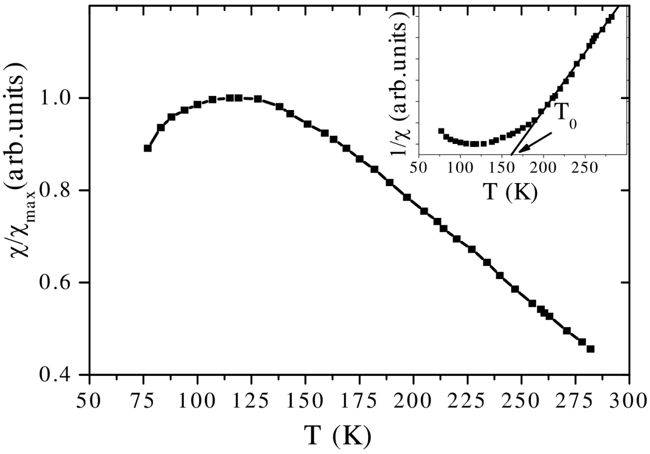


Fig. 1. Temperature dependence of the low-field ac magnetic susceptibility for the Cu–Mn–Al alloy. The inset shows the temperature dependence of the inverse susceptibility for the Cu–Mn–Al alloy

A simple efficient method to determine the magnetic states is the measurement of ac magnetic susceptibility. In Fig. 1, one can see the magnetic susceptibility of Cu–Mn–Al in the temperature range from 77 to 300 K. Its characteristic features are a cusp with the peak value, $\chi_{\rm max}$, at 120 K and a continuous decrease with temperature up to 300 K. The decrease probably indicates the superparamagnetic state. This assumption is supported by the inverse susceptibility versus temperature plot shown by the inset to Fig. 1. According to the Curie–Weiss law, $\chi = N\mu^2/3k_{\rm B}(T - T_0)$, where $\mu$ is the magnetic moment of a particle, and $T_0$ is the transition temperature from the para- or superparamagnetic state into a low-temperature one. As follows from the inset, the linear fit matches satisfactorily the experimental data in the range from 180 to 300 K. The intersection of the fit with the temperature axis defines the transition temperature of about 160 K.

It should be remarked that the cusp in Fig. 1 can correspond to either the Neel point or to the point of transition into the superspin glass state. Since the former case corresponds to a very low $\chi$ magnitude, which unlikely could be detected by low field magnetic

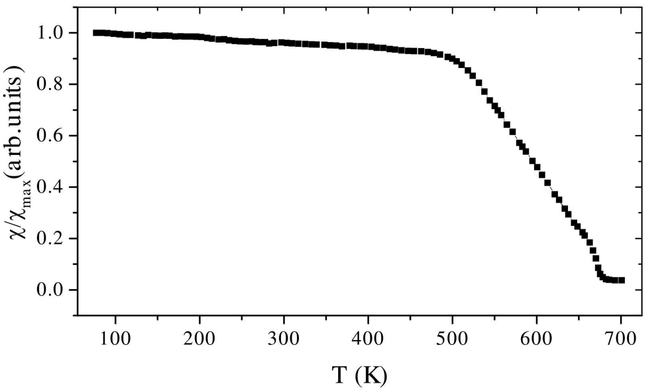


Fig. 2. Temperature dependence of the low-field ac magnetic susceptibility for the Cu–Ni–Fe alloy

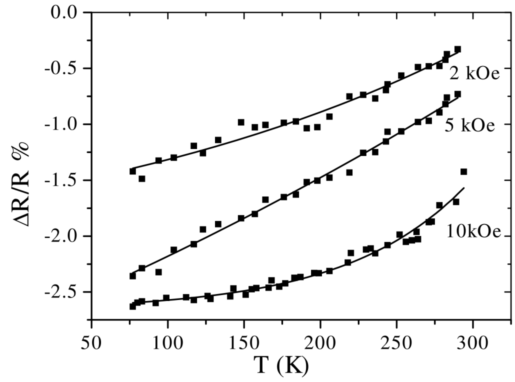


Fig. 4. Magnetoresistance of the Cu–Ni–Fe alloy as a function of the temperature in different magnetic fields

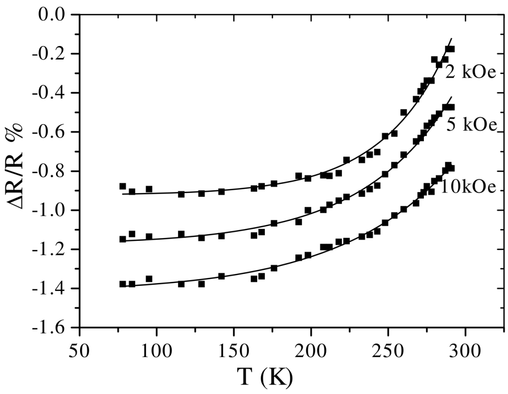


Fig. 3. Magnetoresistance of the Cu-Mn-Al alloy as a function of the temperature in different magnetic fields

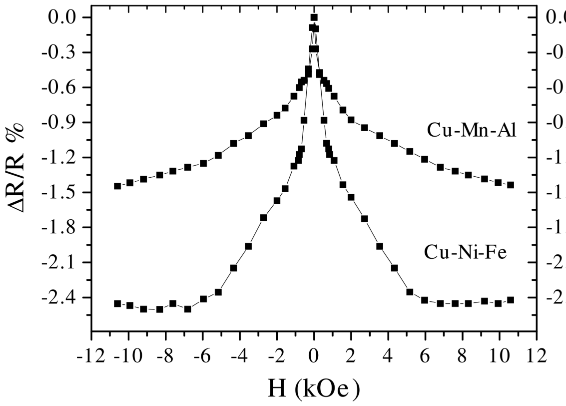


Fig. 5. Magnetoresistance of the Cu–Mn–Al and Cu–Ni–Fe alloys taken at $T = 77$ K under a field parallel to the current

susceptibility measurements, the cusp is indicative of the spin "freezing" (in our case, the superspin glass ordering). Figure 2 demonstrates the same plot for the Cu–Ni–Fe alloy. In this case, indications of the superspin glass state are absent. Instead, the low-temperature state in the system of particles is superferromagnetic, which is supported by a nearly constant run of the magnetic susceptibility with temperature. This state is changed to a superparamagnetic one at about 500 K and then, at 675 K, the magnetic susceptibility drops to zero, probably because it is the Curie temperature for the ferromagnetic phase.

The temperature dependences of the resistance under zero field were featureless; the resistance linearly increased with temperature within the whole temperature interval. Magnetoresistance was plotted only below room temperature (Figs. 3 and 4), since it was low at higher temperatures. Practically, no difference between the measured values of the magnetoresistance under the fields parallel and perpendicular to the current was found, wich indicates a low anisotropic magnetoresistance. If one considers different magnetic states, the magnetoresistance or, as follows from the above, the GMR ratio demonstrates a decrease as the temperature increases in the superparamagnetic state from 160 to 300 K for a Cu–Mn–Al specimen (Fig. 3) and in the superferromagnetic state in the whole temperature interval (Fig. 4) for Cu–Ni–Fe. As regard to the superspin glass state, the magnetoresistance is near constant below 160 K (Fig. 3). The maximal GMR ratios are –1.4% below 140 K for Cu–Mn–Al and –2.6% nearby 77 K for Cu–Ni–Fe in a magnetic field of 10 kOe.

The temperature dependence of GMR measured in this experiment can be interpreted by means of the so-called modified effective exchange interaction model presented in [16] and then extended to granular systems in [17]. According to this model, GMR in granular alloys is a function of both the magnetization which is field-dependent and the magnetic moment or the effective spin of a scatterer (nanoparticle) that is field-independent. In turn, the effective spin of a particle obeys the same temperature dependence as the saturation magnetization on the assumption that the particle is a single domain. It has been shown by the field-cooled magnetization measurements in [10, 18] that the superspin glass state is characterized by the near constant value of magnetization, whereas the magnetization in the superparamagnetic and superferromagnetic states decreases with temperature. It confirms that our temperature dependences of the magnetoresistance are closely associated with that of the magnetization.

It should be noted that, in addition to spin wave excitations which are shown to reduce the magnetic moments of particles [16] and apparently play a dominant role, some spin independent mechanisms such as structural irregularities or/and phonons can contribute to the temperature dependence of GMR.

The measurements of the field dependence of the GMR ratio have been conducted at 77 K. In Fig. 5, both graphs are shown.

Cu–Mn–Al demonstrates the unsaturated character of the GMR ratio in the range of applied fields, which is typical of the superparamagnetic state, although the measurements were taken below the temperature of the transition into a superspin glass state. The increase of the GMR ratio of Cu–Mn–Al with a field is smoother than that of Cu–Ni–Fe. The GMR ratio of the Cu–Ni–Fe alloy saturates at a magnetic field of 7 kOe which is most likely the field wherein specimen reaches the saturation magnetization at a given temperature. According to [4], $\Delta R/R \sim -A(M/M_S)^2$, where $M_S$ is the saturation magnetization and $M$ is the global magnetization which is determined as the magnetization summed over all particles. As is seen from Fig. 5, the GMR ratio in both magnetic states roughly follows this expression.

## 4. Conclusion

The magnetoresistances of the granular alloys Cu–Ni–Fe and Cu-Mn-Al are studied in different magnetic states, namely, in the superparamagnetic, superspin glass, and superferromagnetic ones. It is shown that both the field and temperature dependences of GMR correlate with the type of magnetic ordering in the system of dispersed nanoparticles. The maximal values of GMR, 2.6% for Cu–Ni–Fe and 1.4% for Cu–Mn–Al, are obtained at low temperatures. The superparamagnetic and superferromagnetic states are characterized by a decrease of the GMR ratio with temperature. Below the temperature of the transition to the superspin glass state, the GMR ratio keeps constant.


1. M.N. Baibich, J.M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Eitenne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988).
2. G. Binash, P. Grünberg, F. Saurenbach, and W. Zinn, Phys. Rev. B **39**, 4828 (1989).
3. A.E. Berkowitz, J.R. Mitchell, M.J. Carey, A.P. Young, S. Zhang, F.E. Spada, F.T. Parker, A. Hutten, and G. Thomas, Phys. Rev. Lett. **68**, 3745 (1992).
4. J.Q. Xiao, J.S. Jiang, and C.L. Chien, Phys. Rev. Lett. **68**, 3749 (1992).
5. B. Dieny, V.S. Speriosu, S.S.P. Parkin, B.A. Gurney, D.R. Wilhoit, and D. Mauri, Phys. Rev. B **43**, 1297 (1991).
6. E.P. Butler and G. Thomas, Act. Met. **18**, 347 (1970).
7. M. Bouchard and G. Thomas, Acta Metall. **23**, 1485 (1975).
8. V.V. Kokorin, I.A. Osipenko, S.V. Cherepov, and V.A. Chernenko, *Magnetic States in Cu–Mn–Al System Alloys* (Preprint (IMF, Kiev, 1986) (in Russian).
9. V.V. Kokorin and I.A. Osipenko, Phys. Status Solidi **74**, K147 (1982).
10. O. Petracic, X. Chen, S. Bedanta, W. Kleemann, S. Sahoo, S. Cardoso, and P.P. Freitas, J. Magn. Magn. Mater. **300**, 192 (2006).
11. J.L. Dormann, D. Fiorani, and E. Tronc, Adv. Chem. Phys. **98**, 283 (1997).
12. S. Morup, M.B. Madsen, J. Franck, J. Villadsen, and C.J.W. Koch, J. Magn. Magn. Mater. **40**, 163 (1983).
13. V.F. Puntes, P. Gorostiza, D.M. Aruguete, N.G. Bastus, and A.P. Alivisatos, Nat. Mater. **3**, 263 (2004).
14. V.V. Kokorin, A.E. Perekos, and K.V. Chuistov, in *Structural Mechanism of Phase Transitions in Metals and Alloys* (Nauka, Moscow, 1976) (in Russian), p.131.
15. J.J. Gittleman, B. Abeles, and R. Bozowski, Phys. Rev. **9**, 3891 (1974).
16. J.-Q. Wang, P. Xiong, and G. Xiao, Phys. Rev. B **47**, 8341 (1993).
17. J.-Q. Wang and G. Xiao, Phys. Rev. B **50**, 3423 (1994).
18. V.V. Kokorin, A.E. Perekos, and K.V. Chuistov, Fiz. Metal. Metalloved. **43**, 966 (1977).


Received 05.07.07

## ГІГАНТСЬКИЙ МАГНЕТООПІР В РІЗНИХ МАГНІТНИХ СТАНАХ СИСТЕМИ ФЕРОМАГНІТНИХ НАНОЧАСТИНОК

*С.М. Коноплюк, В.В. Кокорін, Ю.С. Левчук, Л.Є. Козлова*

Р е з ю м е

Вивчався магнетоопір в різних магнітних станах системи наночастинок, що утворилися в твердих розчинах після розпаду сплавів систем Cu–Ni–Fe і Cu–Mn–Al. За допомогою вимірювання магнітної сприйнятливості було ідентифіковано три колективних магнітних стани, а саме суперпарамагнітний, суперферомагнітний і стан макроспінового скла. Отримані температурні та польові залежності магнетоопору показали особливості його поведінки в цих станах.