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Section 6: Nano-structured materials *INVITED*

MAGNETIC INTERACTION AND MAGNETORESISTANCE IN NANOSCALE MELT-SPUN MATERIALS

B. Idzikowski

Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17,
PL 60-179 POZNAN, Poland

The aim of this paper is to describe magnetoresistive properties of two classes of magnetic materials and their relations to their magnetic properties. First class are nanocomposite systems consisting of appropriate fractions of hard and soft magnetic phases. Remanence-to-saturation ratios B_r/J_s larger than ½ in those materials are due to exchange coupling between the grains of both magnetic phases. Microstructural changes of as-spun $Nd_2Fe_{14}B+\alpha$-Fe (20 or 50 wt% Fe) and $Nd_2Fe_{14}B/\alpha$-Fe/$NdCu_2$ ribbons were obtained by subsequent annealing. Exchange-spring behaviour of such magnets affects not only magnetic properties (e.g. saturation moment and remanence enhancement) but also the magnetoresistance. Interesting superposition effects of negative giant magnetoresistance (GMR) and a positive magnetoresistance were found for samples with 10 wt% Cu, which contain $NdCu_2$ - phase. Magnetoresistance in $Nd_2Fe_{14}B$ with 50 wt% Fe is positive and isotropic. Two possible explanations of this behaviour are discussed. Clear evidence for frustrated interaction effects due to magnetic couplings between the Co precipitates were established in Co_2Cu_{98} and $Co_{10}Cu_{90}$, the second class of investigated systems. Both melt-spun giant magnetoresistive alloys show interaction effects even in the ribbons with only 2 at. % cobalt content. Therefore, magnetic properties of these materials cannot be described by the assumption of superparamagnetic behaviour of single-domain particles. The low-temperature peak of the thermomagnetic curves cannot be interpreted as blocking but rather as a spin-glass-like collective freezing transition.

Keywords: Magnetic nanocomposites, Granular magnets, Magnetoresistance, Magnetic interaction, Spin-glass behaviour

1. Introduction

The discovery of giant magnetoresistance (GMR) several years ago still prompts experimental and theoretical investigations in the field of magnetotransport in metallic heterostructures. The effect also has promising and some successful applications. It is now generally accepted, that GMR effects are due to spin-dependent scattering of conduction electrons in or at different ferromagnetic parts of a heterostructure, which can be switched from antiferromagnetic orientation of their magnetization to ferromagnetic by an external field [1]. Thus, the effect relies on small magnetic structures within typical lengths of electronic transport, i.e. the mean free path or the spin diffusion length of conduction electrons. This interpretation of GMR effects both in magnetic granular as well as multilayered systems leads to the question why giant magnetoresistive effects are rarely observed in ferromagnetic composites with randomly magnetized domains. For conventional ferromagnetic materials, giant magnetoresistive effects could arise only by scattering at domain walls. There is a magnetoresistance associated with domain walls, which can be observed, e.g. in iron whiskers. However, the effects are usually small because there are too few domain walls in conventional materials and the wall widths are usually large compared to the electronic transport lengths.

The purpose of the present paper is to describe the magnetoresistance effect due to different magnetic structures in two classes of magnetic materials: (i) composite exchange-spring magnets and (ii) granular systems which are built of small magnetic particles embedded in nonmagnetic matrix.

Magnetic composites consist of a mixture of two or more different exchange-coupled magnetic materials. For enhanced remanence through exchange interactions, the diameters of the grains must be sufficiently small to allow interactions to closely couple single-domain particles of the different constitutents. This can be achieved by producing amorphous melt-spun ribbons, from which the nanocrystalline microstructures result through decomposition and crystallization of various phases. For example, in nanocomposite systems $Nd_2Fe_{14}B+Fe_3B$ [2], $Nd_2Fe_{14}B+\alpha\text{-}Fe$ [3], $Nd_2Fe_{14}B+\alpha\text{-}Fe+NdCu_2$ [4] a smooth magnetization curve is observed due to mutually exchange-coupled grains of hard and soft magnetic phases. The remanence-to-saturation ratios B_r/J_s were found larger than ½, which is a deviation from the Stoner-Wohlfarth (S-W) rule. Obviously, in such a case the S-W assumptions of noninteracting particles with an anisotropic distribution of magnetically easy axes for isotropic systems is invalid. In consequence the enhancement of remanence due to exchange-spring behaviour of such magnets is observed. In these exchange-coupled materials, it is assumed that the magnetization structure is given by so-called "interaction-domains", which comprises several nanocrystalline grains with favourable orientation of their magnetic anisotropies. Thus, the transition region of one magnetization direction to another one in between such "interaction-domains" is confined within a nanoscale microstructure. Thus, such microstructures give rise to various interesting giant magnetoresistive effects, among them are inverse effects where the resistance increases in an increasing field.

The second class of investigated materials are Cu rich granular ribbons containing fine Co particles. By melt-spinning supersaturated solid solutions of Co in Cu matrix can be obtained. Appropriate heat treatment leads to the formation of very fine Co-particles in the beginning of the decomposition reaction. GMR for such heterogeneous structures was found some time after the findings for multilayer structures in granular thin films [5], and also in melt-spun bulk material [6]. The GMR effect is very sensitive to the underlying magnetization distribution in the fine particle system of such granular metals. It was usually assumed that the fine Co-particles are independent and that their magnetism can be described simply by superparamagnetism. However, closer inspection of the magnetic properties and the GMR in such materials uncovers magnetic interaction effects.

2. Experimental

All samples used for the present investigation were prepared by melt-spinning technique in an Ar filled chamber. A single-roller equipment with Cu or Cr wheel and quartz nozzle with rectangular or round shape was used. Details of the technological condition of preparation procedure are described in [3, 4, 7]. From the metastable ribbons after rapid solidification, nanoscale microstructures can be produced by annealing. In the case of exchange-spring materials made from $Nd_2Fe_{14}B$ with 20 or 50 wt.% Fe and small Cu and Zr additions, a mostly amorphous initial state decomposes into the magnetically hard $Nd_2Fe_{14}B$, and into soft α-Fe [3]. Similarly, rapidly solidified samples of $Nd_2Fe_{14}B$ with 10 wt.% Cu addition are partially amorphous but contain already crystalline $NdCu_2$. Annealing leads to the formation of crystalline $Nd_2Fe_{14}B$ and α-Fe [4]. The structure evolution of the samples was investigated by x-ray diffraction (XRD). The mean grain sizes were estimated by means of x-ray diffractometry using Scherrer's method and also from transmission electron microscope (TEM) observations.

Melt-spun Co<u>Cu</u> ribbons consists of supersaturated solid-solution in as-quenched state. Upon annealing, spheroidal Co-particles with fcc-structure are formed, which are coherent with the fcc-Cu matrix. XRD-scans and Co-59 NMR spectra [8] confirmed that Co<u>Cu</u> samples both in as-quenched state and in annealed granular state consists only of fcc-structure. For both types of samples, field and temperature dependence of the magnetization was measured by a vibrating sample magnetometers or by a SQUID magnetometer for fields up to $\mu_0H = 8$ T. Resistivity measurements were made with the four-point technique. Magnetoresistance curves were measured at 10 K for the applied field usually parallel to the sample current up to a field strength 5 T. Some measurements with the field perpendicular to the current were also performed to test for the occurrence of anisotropic magnetoresistance (AMR).

3. Microstructure, Magnetism and Magnetotransport in nanoscale granular materials

3.1. Magnetotransport in exchange-spring magnets

Fig. 1 shows a transmission-electron microscopic picture of an exchange-spring magnet made from $Nd_2Fe_{14}B$ with Fe-addition. The fine-grained structure of such materials predominantly consists of the 2:14:1-phase and α-Fe. The grains have diameters of 10-40 nm. Depending on annealing state, small fractions of a cubic metastable phase $Nd_2Fe_{23}B_3$ among other phases could be found [3]. The materials principle of these exchange-spring magnets [9] is schmatically given in Fig. 2.

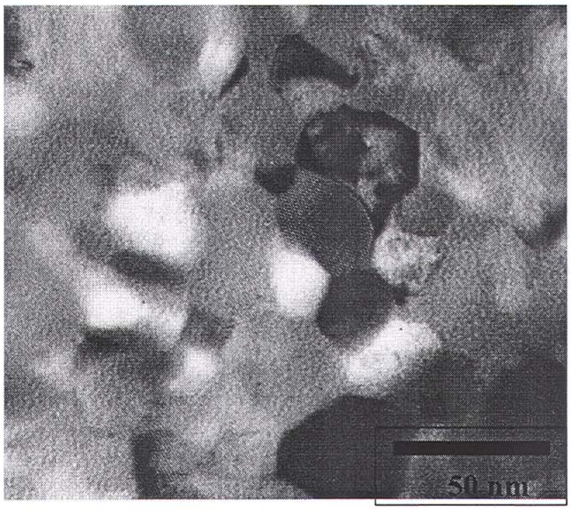

Fig. 1. High-resolution TEM micrograph of optimally head-treated melt-spun $Nd_2Fe_{14}B$+50% wt% α-Fe sample. Clear grain boundaries and for some grains wavy lattice planes are visible.

The hard magnetic phases contribute a high magnetic anisotropy, while the soft Fe phases contribute a high saturation magnetization. Because of the nanoscale microstructure, both consitutents are closely exchange-coupled, and the soft magnetic grains are aligned to the hard-magnetic grains, which provide a skeleton to the magnetic structure. For optimum coercivity the soft grains should have dimensions of the order of the domain wall width of the hard phase about 3-4 nm which is similar to the exchange length in both phases. Then, no two-phase behaviour is found.

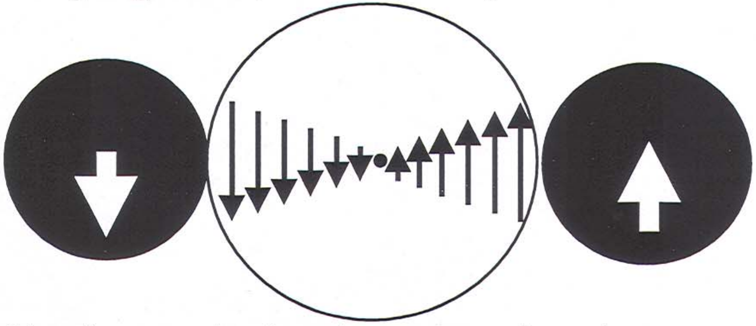

Fig. 2. Schematic representation of an exchange-spring state in two-phase nanocomposite materials.

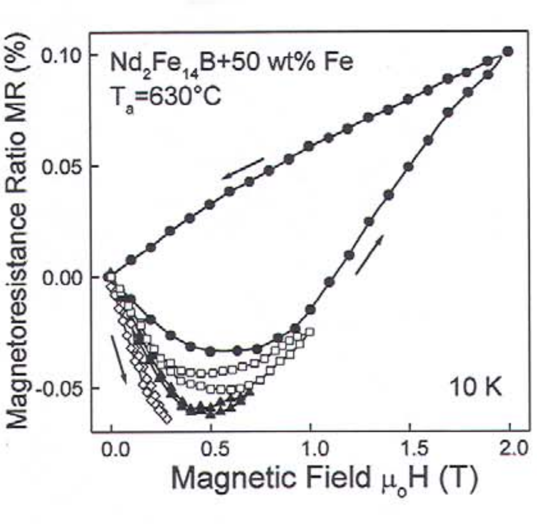

Fig. 3. Reversible and non-reversible behaviour of magnetoresistance in $Nd_2Fe_{14}B$+50% wt% α - Fe.

Between, regions of like magnetization direction, which may be termed "interaction-domains" to distinguish them from conventional domains, a twisting of the local magnetization must occur in soft-magnetic grains as shown in the sketch. Thus, these "interaction-domain walls" are confined by the microstructure. If only the soft-magnetic material is reacting by local distortion of the magnetization in an external demagnetizing field the exchange-spring behaviour is expected. This means, by reducing the external field the magnetization switches back due to the coupling to the hard-phase grains. In such a magnetic hard/soft mixture remanence enhancement occurs. The microstructure is still more complicated as a remaining amorphous interface-phase usually is present between the various crystaline phases.

To demonstrate the complexity of the magnetoresistive effects in these materials, Fig. 3 shows the magnetoresitance ratio $MR(H) = (R(H) - R(0))/R(0)$, where $R(H)$ is the magnetic field dependent resistance, for an annealed sample $Nd_2Fe_{14}B$ with 50 wt.% Fe at low temperature. The sample was cooled in zero-field and resistance was measured for field-cycles with increasing maximum magnetic field. Cycles up to about 0.5 T show a reversible drop of the resistance whereas for larger fields a re-increase and hysteretic behaviour is found. The overall effects are small with 0.1 % compared to usual GMR effects. Previously, for this material it was already shown that this positive (inverse) MR is isotropic and does not saturate up to 5 T. We may compare this to $Nd_2Fe_{14}B$ with 20 wt.% Fe samples, where anisotropic positive or negative MR was found depending on annealing state [4]. In Fig. 4, the magnetoresistance of $Nd_2Fe_{14}B$ with 10wt. % Cu samples in as-quenched and annealed states is shown. In annealed state, a normal GMR-like behaviour with negative magnetoresistance is found. But, there are some peculiarities and hysteresis around the coercive fields H_c of these samples. In as-quenched state, a positive MR is found similar to that observed in $Nd_2Fe_{14}B$+20 wt.% Fe (see [3]).

Various mechanisms for magnetoresistance effects may be present in these materials: (i) The conventional AMR due to spin-orbit scattering takes place within the bulk of magnetized material [10]. (ii) Spin-dependent scattering at the interfaces and in the bulk of the different grains may occur. This may give rise to GMR-like behaviour when the relative direction of the magnetization of the different grains can be reverted in an external field. (iii) There may be magnetoresistance due to spin-dependent scattering of electrons at "interaction-domain walls".

The normal GMR-like behaviour of the annealed samples containing Cu, can be explained by the presence of the $NdCu_2$-phase, which is paramagnetic at 10 K [11]. The specific resistance of the hard phases such as 2:14:1 and of remaining amorphous phase is much larger than that of α-Fe and of $NdCu_2$. Thus, current paths in this material will mainly probe these two phases passing between variously magnetized Fe-grains across non-ferromagnetic $NdCu_2$. The external field aligning the

Fe-grains will reduce the resistance just as in other granular GMR systems. This explains the normal (negative) MR. The magnetization curves for this material shows spring-exchange behaviour and remanence enhancement [4]. Thus, the α-Fe is exchange-coupled to the hard magnetic phases and we may understand the anomalies, i.e. the small increase of the magnetoresistance, around H_c by the mechanism (ii). Near H_c a proliferation of "interaction-domain walls" takes place which may increase the magnetoresistance. In the investigated material, these twisted magnetization structures should be confined to the Fe-grains. Thus, the magnetic state of the hard-phase only indirectly influences the magnetotransport. Recently, Mibu et al. demonstrated such an effect from domain-wall scattering for hard/soft bilayers with current in plane (CIP) [12].

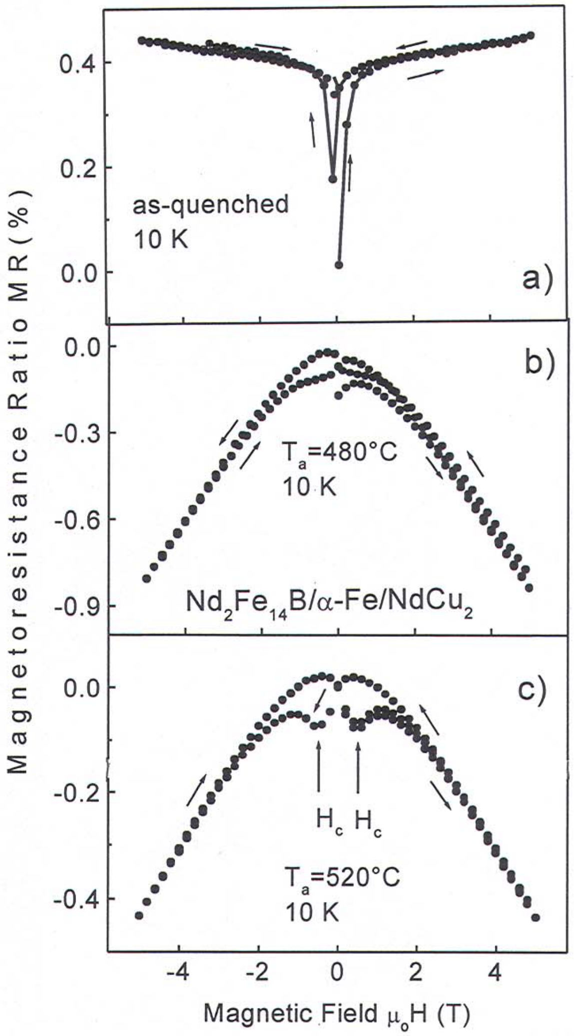

Fig. 4. Magnetoresistance ratio (MR) of melt-spun alloys with nominal composition $Nd_2Fe_{14}B$ + 10% wt % Cu in as - quenched state and after annealing at two different temperatures (measured at 10 K).

The positive MR effects seen for as-quenched material and in Fig. 3 may also be related to scattering due to "interaction-domain walls", especially as it seems related to hystereresis. However, this explanation is not conclusive as an inverse GMR effect may be responsible here. It is generally assumed that the magnetotransport in granular materials resembles that of multilayers with current perpendicular to the layers (CPP) [13]. Then, the transport of electrons with one spin direction can be explained by spin-dependent scattering at interfaces and in the bulk of the different constituents, i.e. by a series of effective resistances along the current path within the spin-diffusion length of conduction electrons [14]. The spin-dependent bulk resistivity of a ferromagnetic material is $\rho_{\uparrow(\downarrow)} = 2\,[1 \pm (-\beta)]\rho^*$, where β is the spin-asymmetry coefficient. The interface resistance between two materials may be written $r_{\uparrow(\downarrow)} = 2\,[1 \pm (-\gamma)]r^*$. If there is electronic transport through two ferromagnetic materials with different signs of β there is a competition between the spin-dependent scattering due to the interface and due to the bulk for one of the materials depending on the sign of spin-asymmetry γ for the interfaces. If one has a series of spin-dependent resistors with different effective spin-asymmetry a positive (inverse) GMR may occur as was recently demonstrated for CPP-transport in FeV/Cu/Co/Cu multilayers and similar systems [15] because the total resistance may be lower for anti-ferromagnetic configurations. Similar effects may occur if a distribution of grain-sizes in a granular material contributes grains with positive and negative spin-asymmtry, because there size of grains with competing bulk and interface spin-dependent scattering decides whether they contribute a stronger resistance for majority-spin (↑) or minority-spin (↓) electrons. The spin-dependence coefficent of the bulk scattering $\alpha = \rho_\downarrow/\rho_\uparrow$ can be estimated from the spin-polarized density of states at the Fermi-level, i.e. $\alpha \approx D_\uparrow/D_\downarrow$. For α-Fe it is known that $\alpha < 1$ [15]. Spin-polarized electron-structure calculations of the local density of states of $Nd_2Fe_{14}B$ indicate that $\alpha > 1$ for almost all Fe-sites in this complicated structure [16]. One may also assume, that in the parent amorphous structure $\alpha > 1$. Thus, there is a plausible mechanism for inverse GMR in very fine-grained $Nd_2Fe_{14}B/\alpha$-Fe whenever the current cannot bypass the Nd-rich parts of the microstructure.

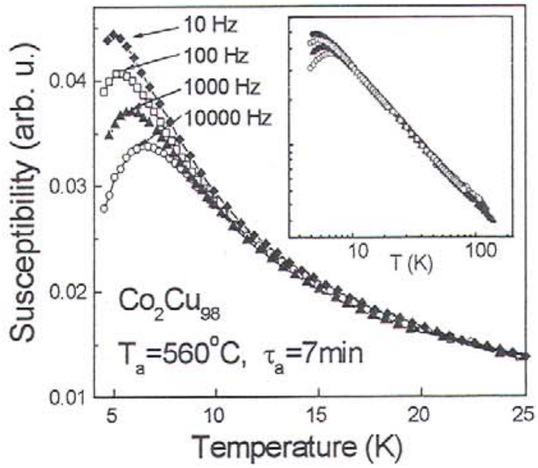

Fig. 5. ac-susceptibility of an annealed granular Co_2Cu_{98} sample at various measuring frequencies. The inset shows the data as double - logarithmic plot. The peak of the susceptibility signals a spin-glass-like freezing.

3.2. Influence of interactions effects on the magnetoresistance behaviour in Co_xCu_{100-x}, x=2, 10

The much simpler microstructure of granular CoCu has only small coherent fcc-Co particles in a nearly depleted Cu-matrix after decomposition of a supersaturated solid solution produced by co-

deposition or by rapid solidification. When the GMR of such systems was first described their magnetic behaviour was entirely explained by superparamagnetism and blocking of independent Co-particles [5]. However, detailed investigations show that there is substantial influence of magnetic interactions between these particles. These interactions modify the magnetoresistive properties of the system as they introduce correlations between the magnetic moments of different ferromagnetic particles, which scatter the conduction electrons. The interaction effects can be studied in particular by dynamic properties as was shown in Refs. [17, 18] for Co_xCu_{100-x}, x=2, 10. The spin-glass-like freezing of a Co_2Co_{98} sample is highlighted in Fig. 5. An analysis of the frequency dependence of the ac-susceptibility clearly disproves superparamagnetic blocking for these materials [18]. Very slow relaxation phenomena found for the resistivity of $Co_{10}Co_{90}$ cooled below this freezing the glassy dynamics could be asserted [17]. Similar effects could also be found for granular Fe<u>Cu</u> [19]. In Fig. 6, it is shown that a creep of the resistivity following zero-field cooling occurs also in Co_2Co_{98}.
This further corroborates the existence of (frustrated) interactions between the Co-particles in such granular metals even at low volume fraction of the ferromagnetic constituent.

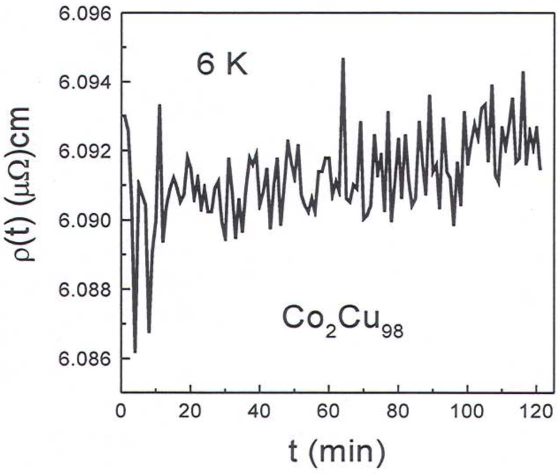

Fig. 6. Slow creep increase of the resistivity for the annealed Co_2Cu_{98} sample after zero-field-cooling below the spin-glass-like freezing (see Fig. 5).

4. Discussion and conclusions

The length-scale pertinent to GMR effects and similar effects is set by electronic transport. Thus, as we have seen nanoscale materials are necessary for finding such effects. Usually, antiferromagnetic configurations of ferromagnetic constituents such as layers or grains show higher resistance which can be lowered by aligning them in an external field. However, in the exchange-coupled materials, the occurrence of domain-walls may lead to an increase of the resistance with increasing field. Then the details of magnetic interactions and configurations become important. The effects seen for the exchange-coupled nano-composites still are rather small. However, it is known from nano-constrictions of ferromagnetic materials that confining domain-walls to very small dimensions may lead to very high magneto-resistance effects [20]. The design of granular materials with a percolating network linked by such nanocontacts may be an interesting challenge.

The general principle of normal GMR in artificial heterostructures is known for long times in metamagnetic compounds, which undergo a transition from antiferromagnetic configurations to ferromagnetism in an external field. Therefore, it is interesting to study the magnetoresistance of such compounds, which is usually large but sets in only above the metamagnetic critical field. Here again the interplay between magnetic interactions and magnetoresistance becomes important and can be modified by certain microstructures. Recently, we showed that microstructures built from a metamagnetic $DyCu_5$, ferromagnetic $DyCu_7$ and Cu may shows strong magnetoresistance already below the metamagnetic critical field [21, 22]. Also e.g., in our former experiments, we showed that additions of rare-earths to granular Co<u>Cu</u> may lead to important modification of their magnetoresistance [23].

As was shown in this paper a contribution of "interaction domain walls" to the inverse-like GMR observed in the 2:14:1-based systems is likely. However, a true inverse GMR due to the electronic structure of $Nd_2Fe_{14}B$ as opposed to that of α-Fe cannot be ruled out.

Finally, the very high sensitivity of magnetoresistance to underlying microstructure and magnetic configurations opens insight into these properties, which would be difficult to probe by other measurements. This was demonstrated by the finding of spin-glass-like slow relaxation for the resistivity of Co<u>Cu</u> at low volume fraction of Co.

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