AC-granular magnetoresistance effects in systems with organic matrices

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ABSTRACT

We present transport measurements carried out for granular systems consisting of Co nanoparticles embedded in organic and well conducting matrices. Magnetoresistance effect amplitudes of more than 60% were obtained at room temperature. Transport measurements with alternating current (AC) were found to enhance both long-term stability and signal-to-noise ratio of the MR curves. In order to investigate the kind of conductivity, IV characteristics were studied at temperatures above and below the freezing point of the gel.

Keywords: magnetic nanoparticles, granular magnetoresistance effect, alternating current, transport measurement

1 INTRODUCTION

The giant magnetoresistance (GMR) effect was originally studied in magnetic multilayer systems [1, 2]. Later, it was also reported within granular systems where ferromagnetic granules are embedded in a metallic matrix [3, 4]. We have replaced the matrix of previous granular systems by a conductive nonmagnetic gel. Transport measurements with direct current (DC) revealed GMR effects of more than 60%, which is far above the values known from common granular systems [5, 6]. AC transport measurements were found to clearly improve the long-term stability of this effect amplitude.

2 SAMPLE PREPARATION AND EXPERIMENTAL SETUP

The Co nanoparticles employed in this work are commercially available. They are prepared by a modified flame synthesis method and are carbon coated. The deposition of the carbon shell was achieved by adding acetylene to the nanoparticle forming process. The particles feature a broad size distribution, which was obtained by transmission electron microscopy (see Fig. 1 (a)). A mean diameter of the particles of about (17.9 ± 18.7) nm was revealed by a statistical analysis. The ferromagnetic behavior of the particles was proved by Alternating Gradient Magnetometer (AGM) measurements at room temperature (Fig. 1 (b)). GMR samples were prepared by dispersing nanoparticles in conductive liquid matrices [8]. Therefore, hydrogels different in conductivity and viscosity were tested.

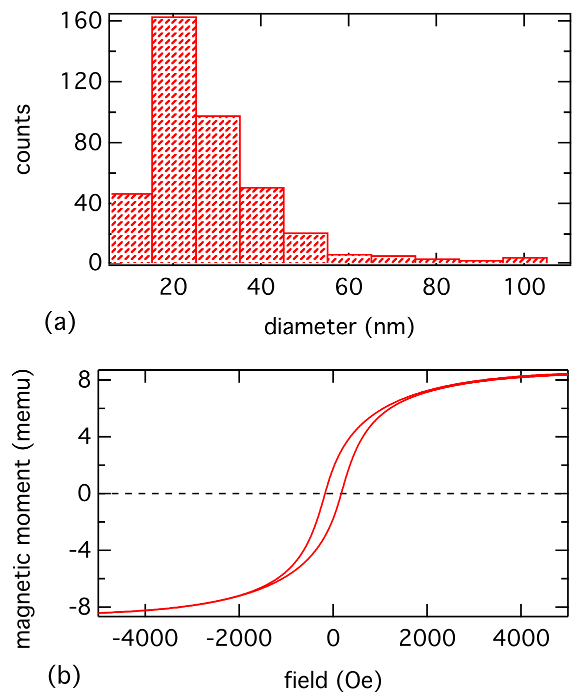

Figure 1: Subfig. (a) gives the size distribution of the Co nanoparticles obtained by TEM. The particles are broadly distributed with a mean value of 18 nm. AGM measurements at room temperature revealed ferromagnetic behavior of the particles (b).

A crucial point regarding the transport measurements is the conductivity of the matrix. Drying of some of the hydrogels over time resulted in a loss of the conductivity and hence a decreasing effect amplitude. With the gel completely dried no MR effect was measured [8]. This difficulty was overcome by the use of agarose or alginate gel. Those biogels feature a liquid-solid transition. For the sample preparation agarose gel is heated up to more than 75°C to attain the transition to liquid. After stirring in the particles, the sample can be filled in a vessel. Cooling down again initializes the gelling process. For the creation of particle chain fragments in the sample, the sample can simultaneously be exposed to a homogenous magnetic field. Alginate gel, on the other hand, is prepared at room temperature by mixing alginates with a curing agent. For both biogels, particles are fixed in the gel environment after the transition to solid. In the measurement setup, the sample is contacted from above with four needles that are configured in-line. The distance between two needles is 4 mm. Via the two outer needles the current is injected, while the inner ones are used for the voltage measurement. Transport measurements are carried out by a 4-point-probe method at room temperature. A constant direct current of 5 μA is applied parallel to a magnetic field. The magnetic field is increased uniformly from −2000 Oe to 2000 Oe and then decreased in the same way while the voltage is recorded. The magnetoresistance is calculated according to

$$GMR = \frac{\Delta R}{R_{\min}} = \frac{R_{\max} - R_{\min}}{R_{\min}} \qquad (1)$$

where R_{max} is the maximum resistance, which in granular systems is obtained for no external magnetic field, when the magnetic moments of the single particles are statistically distributed leading to the highest degree of disorder. R_{min} is the minimum resistance, which results from the alignment of the single moments in the direction of the magnetic field.

3 RESULTS AND DISCUSSION

3.1 DC transport measurements

First transport measurements were carried out with DC [8]. Fig. 2 shows results for the Co nanoparticles in agarose gel. For the sample without chain fragments a MR effect of about 13% was achieved (dashed line). Chain fragments in the sample oriented in the direction of the external magnetic field and the current were found to strongly increase the effect amplitudes. With chain fragments in the sample an effect amplitude of about 68% was measured (solid line).

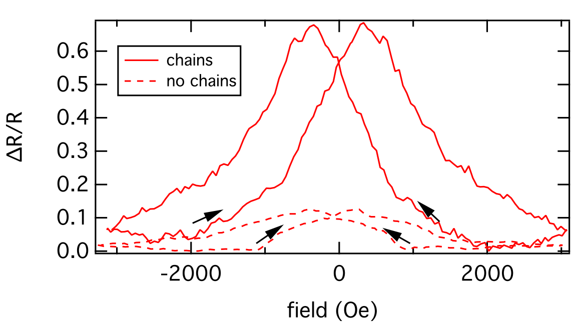

Figure 2: DC transport measurements for Co nanoparticles in an agarose gel matrix. For the sample that had been exposed to a magnetic field during gelling process (chains), particle chain fragments could evolve resulting in a higher effect amplitude than for the sample with no field applied during gelling process (no chains).

Fig. 3 (a) and (b) show the corresponding agarose-particles samples after the measurement. For current applied parallel to the magnetic field, chain fragments orientated in the direction of the external field result in an uniaxial anisotropic particle density in the implied direction. Increased spin-dependent scattering along the current path consequently leads to large effect amplitudes [9].

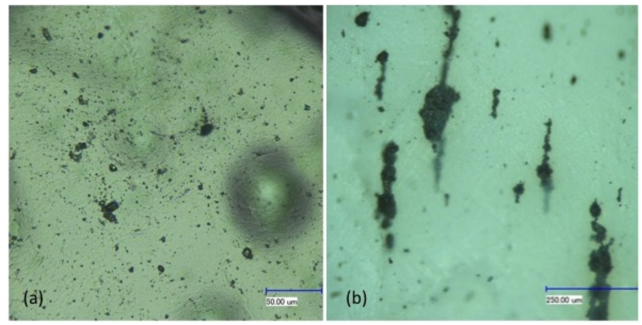

Figure 3: The figure displays a sample of Co nanoparticles in agarose gel with no magnetic field applied during gelling process (a) and a sample of Co nanoparticles in agarose gel with field applied during gelling process so that particle chain fragments could evolve (b). The pictures were taken after the transport measurement by an optical microscope.

3.2 AC transport measurements

During measurements with DC electrolysis effects might occur in the matrix. Fig. 4 shows IV characteristics measured for pure agarose gel. The red curve corresponds to the DC measurement. Electrolysis leads to changes in ion concentration of the matrix. Additional ions at the electrodes that are reduced and oxidized, respectively, thus contribute to the current and lead to reduction waves, which can clearly be observed at about -0.1 V and 1.2 V. With respect to the transport measurements, this leads to unstable voltages and a low reproducibility of effect amplitudes (compare Fig. 5).

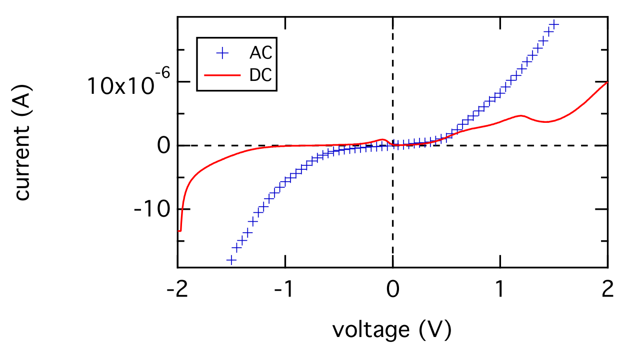

Figure 4: IV characteristic of pure agarose gel measured with DC and AC. While waves due to chemical reactions in the matrix can be found for the DC IV-curve, the AC IV-curve is clearly symmetric to the origin.

By the use of AC, the polarity of both electrodes is reversed periodically. When a frequency higher than the timescales of processes at the electrodes is chosen, electrolysis can be suppressed. For AC measurements, a voltage sequence was applied computer-operated. Starting at zero V the voltage was increased up to 2 V in steps of 50 mV with always a positive voltage followed by the corresponding negative value (0, +50V, -50V, +100V, -100V, ...). The frequency was about 3 Hz. The resulting plot of such a measurement for pure agarose can be seen in Fig. 4 (blue markers). The AC characteristic does not show any waves and is clearly symmetric to the origin. AC transport measurements were performed by employing an alternating voltage with a frequency of 110 Hz. Stability and reproducibility of the MR effects could be enhanced significantly. High effect amplitudes were achieved over a long period of time at a high signal-to-noise ratio (Fig. 5).

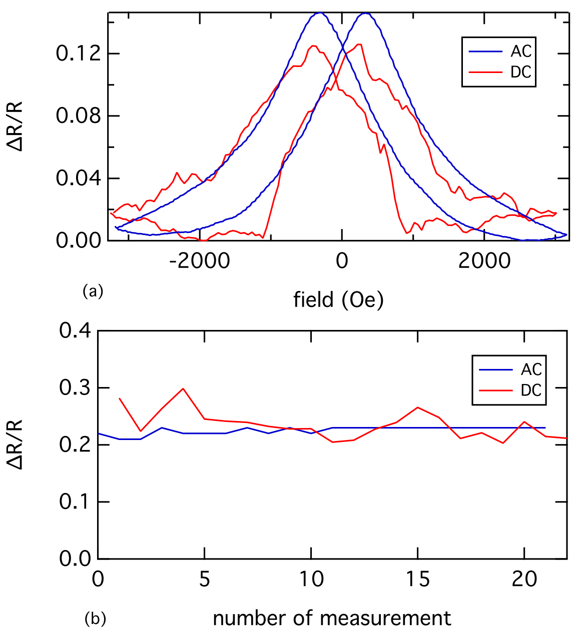

Figure 5: Subfigure (a) displays the DC transport measurement of a sample of Co nanoparticles in agarose gel in comparison to the AC transport measurement. For AC a higher signal-to-noise ratio was achieved. In subfigure (b) the effect amplitudes measured for Co particles in agarose gel are plotted versus the number of iterative measurements for DC and AC, respectively.

3.3 Conductivity

While the nature of conductivity is electronic in the chain fragments of Co nanoparticles, it is mainly ionic in the pure gel, which was found by temperature dependent IV characteristics. For measurements at low temperatures a closed cycle Helium cryostat (Oxford Cryodrive 1.5) with a temperature range of 13 K to 33 0K was used.

Starting from 304 K a sample of Co nanoparticles in 2% agarose at a mass concentration of c=0.03 was cooled down to 247 K. In steps of 2K the IV characteristics were measured with AC. Afterwards the cryostat was warmed up step-wise and measurements were carried out in the same manner.

Starting from 302 K, the recorded IV characteristic is clearly non-linear (Fig. 6). Above the freezing point of the gel, there are two contributions to conductivity: The ionic conductivity and the conductivity mediated by electrons. Due to the ionic part, the resulting IV characteristics are non-linear. It is remarkable that with decreasing temperature the curve slightly starts to flatten and finally gets ohmic at about 275 K (inset of Fig. 6). Due to a shift between measured and actual temperature this corresponds to the freezing point of 273 K. At this temperature, ions are no longer contributing by an additional cathodic or anodic current as the energy for these processes is too low. We now only see the electronic fraction, which is about three orders of magnitude smaller. The possibility that electronic conductivity solely takes place in long particle chains that range from one electrode to the other can be ruled out by the fact that dried samples are no longer conductive [8]. When warming up, the ohmic IV characteristic reaches its prior non-linear form above the freezing point.

From the IV measurements the conductivity was calculated. Fig. 8 displays the natural logarithm of the conductivity in dependency of the reciprocal temperature. The leap in conductivity is attributed to the freezing point of the gel.

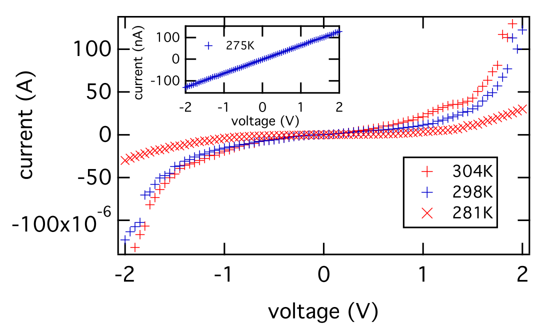

Figure 6: The figure displays the IV characteristics of a Co-agarose sample measured with AC during the cool-down recorded for 304 K, 298 K and 281 K, respectively. Starting from 304 K it shows a non-linear behavior that slightly starts to flatten. The characteristic in the inset measured at 275 K is clearly ohmic.

The most evident proof of ionic conductance is the detection of electrolysis or more precisely its products. In addition, the temperature dependence of ionic conductivity, generally obeys Arrhenius behavior. Mathematically, it is represented by [10]

$$\sigma = \sigma_0 \cdot \exp\left(-\frac{E_a}{k_B T}\right) \quad (2)$$

with E_a the activation energy, σ_0 a preexponential factor, which represents the conductivity for T tending to infinity, and k_B the Boltzmann constant. The statistical mechanical interpretation of that equation is that the mechanism of ion transport is a thermally activated process with an energy barrier of size E_a that must be overcome for ionic conduction to occur. Implying equation (2) a fit for temperatures above the freezing point is in good agreement with the experimental data. An activation energy of (459.0 ± 24.5) meV was revealed.

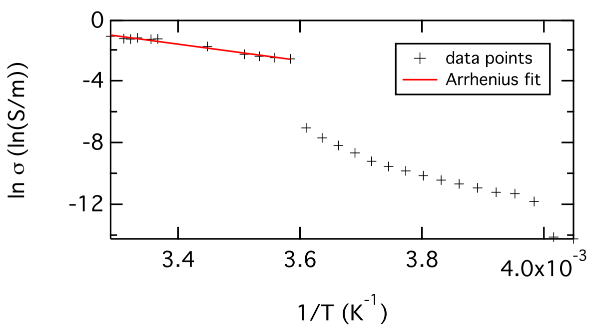

Figure 7: The natural logarithm of the conductivity of the Co-nanoparticles-agarose gel is plotted versus the reciprocal temperature. The leap in conductivity is due to freezing of the matrix and, associated with that, the decrease of ionic conductivity.

4 CONCLUSION

High MR effects were found for Co nanoparticles in biogel matrices. An enhancement of stability and signal-to-noise ratio could be attained by transport measurements with AC leading to the suppression of electrolysis effects. Conductivity in the biogel above the freezing point was found to be mainly ionic with an activation energy of about 459 meV. Regarding future applications, the possibility of printing gel will allow for the development of granular gel-GMR sensors. Such sensors could be realized without the customarily used sputtering procedures for metallic matrices or employing photo- or e-beam lithography [7]. Together with the fact that alginate- or agarose gels are readily available at low cost, this will result in a fabrication more rapid and less expensive compared to conventional devices. Moreover, the large effect amplitudes ensure high sensor sensitivity and the mechanical flexibility of the matrix might additionally open up new fields of application.

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