Origin of the magneto–thermogalvanic voltage in cluster-assembled metallic nanostructures

To the Editor — In their September 2006 article in *Nature Materials*, Serrano-Guisan *et al.* describe magneto-transport and thermoelectric measurements of magnetic nanoparticles in a metallic matrix[1] that exhibit giant magneto-resistance[2,3] (GMR). In such systems the resistance is lowest in large magnetic fields when the magnetic particles are aligned. As the applied field is reduced, the magnetization directions of the particles become random due to local variations in the anisotropy, interactions and thermal fluctuations, resulting in increases in the resistance[2,3]. For small, low-anisotropy particles, the dominant process for randomizing is thermal activation known as superparamagnetism.

The GMR results of Serrano-Guisan *et al.* are consistent with previous measurements of granular systems. Interestingly, when the authors measure the magnetic thermogalvanic voltage (MTGV) — the voltage change to an oscillating temperature — they observed a giant magnetic response of 500%, nearly two orders of magnitude greater than the normalized GMR response. The authors argue that the MTGV response measures a spin-dependent transport mechanism counter to most descriptions of GMR[1,4]. This conclusion was based, in part, on the experimental observations that the sign, magnitude, field dependence and temperature dependence of the MTGV signal are qualitatively different from the corresponding GMR response. In this correspondence we argue that these observations can be understood from the known physics of GMR and superparamagnetism.

The resistivity of granular magnetic systems is well described by:

$$\rho = \rho_0 + \rho_M(1-M^2) \qquad (1)$$

where ρ_0 is the residual resistivity and the second term depends on the global magnetization (M) scaled by a magnetic scattering coefficient[2] (ρ_M). For a non-interacting collection of superaparmagnetic particles M is often estimated by the Langevin function

$$M = \coth(X) - 1/X \qquad (2)$$

where $X = \mu H/k_B T$, μ is the total moment of the magnetic particles, H is the applied field and k_B the Boltzmann constant. Equations (1) and (2) provide a simple description of resistivity changes to variations of both H and T variations (ρ versus X, in Fig. 1a) and T ($\Delta\rho$ versus X, Fig. 1b). As can be seen from Fig. 1a, the GMR response (that is, ρ versus H) is negative and asymptotically decreases towards saturation as observed experimentally. In contrast, $\Delta\rho$ (Fig. 1b), which would be detected in an MTGV measurement is zero at $H = 0$, positive for small fields, reaches a maximum at $X = \pm 3$ and then decreases for higher fields.

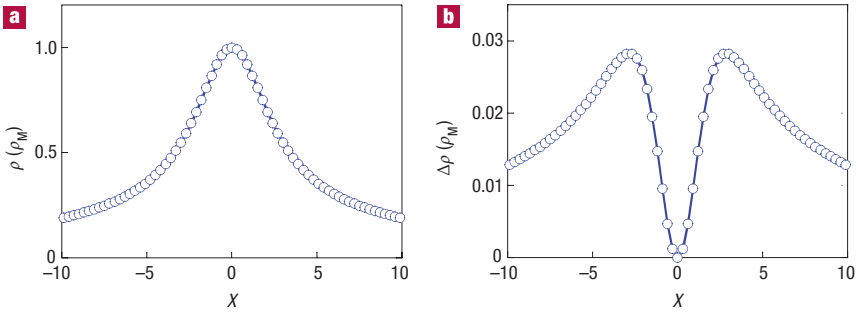

Figure 1 The calculated magneto-thermal transport response assuming a collection of independent superparamagnetic particles of moment *m* in a metallic matrix. a, GMR response (ρ versus $X = mH/k_BT$) calculated from equations (1) and (2) for $-10 < X < 10$ assuming $\rho_0 = 0$. **b**, Difference between ρ calculated at 15 K and 14 K for common H values (corresponding to the experimental conditions).

The curve in Fig. 1b reproduces many of the features of the experimental MTGV data in ref. 1. For the sample with 15 atoms per cluster, X should be in the range ±1.1 (assuming $2\mu_B$ per Co atom, $T = 14$ K and maximum field of 0.8 T). For this range of X, both ρ and $\Delta\rho$ are monotonic with increasing H and with opposite signs, whereas for larger magnetic particles one expects the non-monotonic response of Fig. 1b as seen experimentally. For the smallest particles the reported GMR at $H = 0.8$ T is ~0.8 ohms, which corresponds to 6.4 mV (ref. 1). The corresponding MTGV response is about 6 μV. From Fig. 1, the calculated $\Delta\rho$ response is about 2% of the GMR signal, which would correspond to roughly a 130-μV MTGV response. Although much larger than the measured MTGV signals, it suggests that such signals are certainly possible from the combination of thermal activation and GMR. Finally, the MTGV data in ref. 1 was normalized to the $H = 0$ value to determine the 500% response. Within this model the calculated magnetic response of $\Delta\rho$ is zero at $H = 0$. The measured MTGV response at $H = 0$ would then result from the temperature dependence of ρ_0, which at 14 K is quite small. The normalized MGTV can then, in principle, be arbitrarily high, limited only by the temperature dependence of the residual resistivity. For higher temperatures the MTGV signal arising from the temperature dependence of ρ_0 would overwhelm the magnetic signals as seen experimentally.

In conclusion, the experimental results of Serrano-Guisan *et al.* show interesting thermal-magnetic responses of granular systems. We believe many of the observed results can be understood from a combination of GMR and superparamagnetism (or more generally a temperature-dependent response of the magnetic order) and may not require a new description of magneto-transport. This model reproduces all the qualitative features of the reported data. Quantitative differences are expected and reflect the simplicity of the Langevin description that doesn't include particle distributions, anisotropy or interactions. However we believe that this type of measurement, which probes the magnetic response to thermal excitations, is a unique tool for studying the important role of thermal energies in nanomagnetic systems.

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Authors' response: What we called magneto-thermogalvanic voltage (see, for example, ref. 1) is, in the case of granular systems, the experimental determination of the derivative of the resistivity with respect to temperature. It suppresses the large field- and temperature-independent scattering processes. Its advantage is comparable to that of, for example, dI/dV experiments that reveal conductivity features otherwise undetectable by direct measurements of current versus voltage. We wish to clarify a few points about our samples and measurements.

First, the samples of the study under discussion[2] were prepared at a cobalt loading of 8%. They have a magnetic field response that, for each given T, might be roughly approximated by a Langevin-based model. However, SQUID magnetometry[3] as well as the GMR data in Fig. 4b of our article, show that they were not superparamagnetic (see also ref. 4).

Second, the dR/dT measurements challenge the models of transport more visibly than the GMR data. For example, Fig. 1a shows GMR data for a dilute sample (0.8%) consisting of cobalt clusters of aproximately 40 atoms in a silver matrix, measured at 3 K. Also shown is a fit according to the superparamagnetic model as used by Fullerton and Mangin in their comment, that is, $\Delta R/R \propto ((1-\mathrm{L}(H, T)^2)$ with L(H, T) the Langevin function. Despite this low concentration, the superparamagnetic description is not adequate[4]. However, a reasonable fit to the GMR data can be obtained (see ref. 4). In Fig. 1b, the measured derivative of the resistivity (dR/dT) clearly departs from the calculated derivative based on the Langevin fit of Fig. 1a.

We should also add that given that the current densities were of the order of $<10^4$ A cm^{-2}, we would not expect any effect from other mechanisms, deriving, for example, spin-torque phenomena[5,6].

Regarding the comments by Fullerton and Mangin on measurements of the variation of resistance with temperature, we agree that this type of data should help evaluate better models of spin-dependent transport, in particular the extent to which one should include contributions such as spin-transfer torque[5,6] interface spin-flip scattering[7], spin mixing[8] and spin-disorder scattering[9,10].

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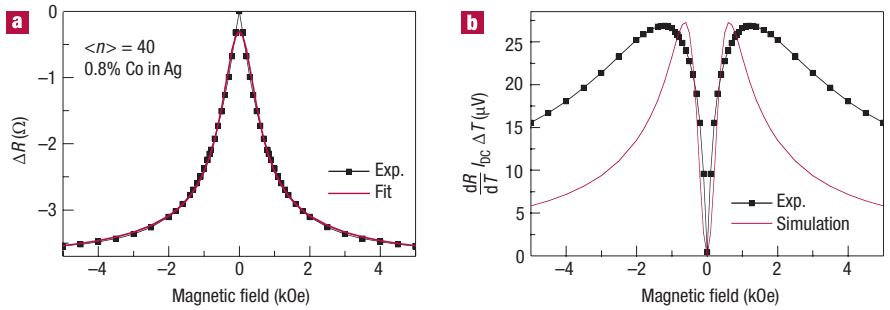

Figure 1 Superparamagnetism model challenged by differential resistance measurements. **a**,**b**, Measurements of the magnetoresistance ΔR (**a**) and $(\mathrm{d}\Delta R/\mathrm{d}T)I_{DC}\Delta T$, where ΔT is the amplitude of the temperature oscillation (60 mK) and I_{DC} the applied current (1 mA) (**b**) for a sample containing cobalt clusters with $<n> = 40$ atoms in a silver matrix with 0.8 at.% Co as measured at 3 K. The red curves exhibit a fit according to the super-paramagnetic model (**a**) and the corresponding temperature derivative (**b**).

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Origin of the energy bandgap in epitaxial graphene

To the Editor — In their recent *Nature Materials* article "Substrate-induced bandgap opening in epitaxial graphene"[1], Zhou *et al.* present thickness-dependent electronic bandstructure measurements (ref. 1, Fig. 2a–c) by angle-resolved photo-emission spectroscopy, with similar data to those reported by our group previously[2]. From the data, Zhou *et al.* assert that chemical bonds to the substrate break the 'A–B' symmetry of the graphene lattice, opening a gap in the bands near the Dirac energy E_D. This contradicts our observation of a kink at E_D related to electron-plasmon scattering[3], a conclusion supported by the strong doping-dependence of the kink and by theory[4,5]; it also contradicts scanning tunnelling microscopy (STM) measurements and theory, which find no such gap[6,7]. Zhou *et al.* also assert that gaps observed in multilayer graphene are dominated by this same substrate effect, and not by the electric field across the film as proposed by Ohta and colleagues[2,8]. In advancing these claims, Zhou *et al.* have misrepresented our momentum distribution curve (MDC) self-energy analysis[3] as naively including artefacts from tails of far-away energy distribution curve (EDC) peaks. Actually, our MDC and EDC peaks always coincide as a consequence of our self-consistent treatment[9] and careful alignment. Such a self-consistent treatment is much more informative than arbitrarily drawn dispersion lines that purport to show a gap.

A substantial case against substrate-induced gaps in graphene for our samples[3] is reported elsewhere[9]. Both electron microscopy[10] and STM studies[6] showed large, uniform graphene terraces. In particular, the strong intensity anisotropy of the Fermi surface (Fig. 1a, upper) imposes a strict limit on the gap due to A–B symmetry breaking (from any source)[9] to a value much smaller than the observation by Zhou *et al.*, and to the size of the lifetime-broadening due