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Magnetotransport properties of magnetic granular solids: The role of unfilled *d* bands

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We calculate the magnetoresistance and magnetothermopower of magnetic granular solids. Contrary to previous theories of the giant magnetoresistance (GMR), we demonstrate that the unfilled *d* bands of magnetic grains play an essential role in the transport properties of these systems. Our results relate GMR and magnetothermopower to microscopic and geometric quantities, and provide a natural explanation for many experimentally observed features, such as the $(M/M_s)^2$ dependence of the GMR, the giant magnetothermopower and its $1/\rho$ scaling behavior, and the absence of negative GMR in rare-earth–nonmagnetic structures.

The discovery of a novel magnetotransport phenomenon of giant magnetoresistance (GMR) in a variety of antiferromagnetically coupled, transition-metal multilayers has attracted much attention.[1-5] Recent experiments have shown that this extraordinary GMR also occurs in magnetically inhomogeneous media containing nonaligned ferromagnetic grains of microscopic size.[6,7] As in their multilayer counterparts, the resistivity drops several tens of percent when the magnetic field orients the magnetic moments. These experiments open a new class of systems for understanding the underlying physics of GMR.

Previous theoretical explanations of GMR have focused on the existence of spin-dependent potential scattering at the interfaces or in the bulk of ferromagnetic layers.[1,6,8-11] In addition to the limitation of being valid only for layered systems, such theories totally ignore the existence of the unfilled *d* bands in the transition metal constituent. While these models can *fit* GMR data for layered systems reasonably well (sometimes using physically nontransparent parameters),[8,9] they are completely inadequate to explain certain other features, such as a very small magnetoresistance in rare-earth structures,[7,12,13] the giant magnetothermopower (GMTP), and its strong correlation with the GMR.[14-16] Given the fact that all systems that show appreciable negative MR consist of transition metal entities surrounded (or separated) by a nonmagnetic metal, and considering the special role played by the unfilled *d* bands in transition metals,[17] it should not be surprising that the electronic structure must be taken into account in order to reach a comprehensive understanding of these systems.

In this paper, we present a theoretical study of the magnetotransport properties of magnetic granular solids. Our model differs substantially from Refs. 8 and 9. We show that the ordinary spin-dependent *s*-*s* scattering arising from a spin-dependent potential *cannot* by itself coherently explain GMR, GMTP effects, as well as other features. Moreover, we demonstrate that the asymmetric density of state (DOS) for majority- and minority-spin *d* bands in the transition metal constituent gives rise to strong spin-dependent scattering (even in the absence of spin-dependent scattering potential), and is responsible for the novel magnetotransport properties in these systems. Our approach treats the GMR and the GMTP on an equal footing, and explains many experimentally observed features. In particular, we obtain *closed* expressions for the GMR and the GMTP of the granular systems. These formulas relate the magnetotransport properties to microscopic and geometric quantities, and are in accordance with experimental measurements.

We confine our discussions to low temperatures and neglect magnon and phonon scattering. The former assumption limits our consideration to scattering processes that do not cause spin mixing.[18] The current in the sample is assumed to be carried by the *s* electrons which are scattered by randomly distributed impurity potential $V^B=\sum_p\sum_j v^B(\mathbf{r}-\mathbf{r}_j-\mathbf{R}_p)$, as well as by interfacial scattering potentials $V^S=\sum_p\sum_j v^S(\mathbf{r}-\mathbf{r}'_j-\mathbf{R}_p)$, where $\mathbf{R}_p$ is the position of granule p, $\mathbf{r}'_j$ is the position of a bulk or surface scattering center relative to $\mathbf{R}_p$. The *s* electrons can be scattered into either *s* band (*s*-*s* scattering) or *d* band (*s*-*d* scattering) when scattered either at interfaces or inside magnetic grains.[17] We focus here on situations in which the sizes of magnetic particles and their separations are less than electron mean-free path. This simple case deserves a detailed study because analytical expressions for GMR and GMTP can be obtained, which yield a clear physical picture and permit a direct comparison between theory and experiment. In the following we consider each spin component and proceed in the context of the conventional two-current model, based on the Boltzmann equation.[18]

Magnetic granular solids are inhomogeneous systems. However, when the granules are distributed randomly, and when their sizes and separations are less than the mean-free path of conduction electrons, the relaxation rates for each spin channel can be obtained by adding the contributions of individual grains. We choose a space-fixed frame *xyz* and specify spin-↑ and -↓ with respect to the global quantization axis *z* along the external magnetic field **H**. The relaxation rate $1/\tau^p_\sigma$ due to the

pth granule is given by[18]

$$\frac{1}{\tau_\sigma^p}=\sum_{\sigma'}\sum_{\mathbf{k}'}\left[1-\frac{\mathbf{k}\cdot\mathbf{k}'}{k^2}\right]P(\mathbf{k}'s\sigma',\mathbf{k}s\sigma)+\sum_{\sigma'}\sum_{\mathbf{k}'}P(\mathbf{k}'d\sigma',\mathbf{k}s\sigma)\quad(\sigma=\uparrow,\downarrow)\,, \tag{1}$$

where $P(\mathbf{k}'l'\sigma',\mathbf{k}l\sigma)$ is the transition rate between states $(\mathbf{k}'l'\sigma')$ and $(\mathbf{k}l\sigma)$ due to the interface and bulk scattering of the pth granule. Note that we assume that each s-d scattering event contributes to the relaxation rate irrespective of $\mathbf{k}\cdot\mathbf{k}'$.[18] To proceed, we further introduce a frame $x'y'z'$ attached to the pth granule with z' along its magnetic moment $\mathbf{m}_p$. The $x'y'z'$ frame is related to the global xyz frame by the Euler angles $(\alpha_p,\beta_p,\gamma_p)$, where β_p is the angle between $\mathbf{m}_p$ and $\mathbf{H}$.[19] In the local $x'y'z'$ frame an interfacial or bulk scattering potential in the pth granule is written as

$$v=\begin{bmatrix}v_+ & 0\\ 0 & v_-\end{bmatrix}. \tag{2}$$

Hereafter we omit the superscripts B or S of v whenever it is not necessary to distinguish v^B and v^S. For generality we have assumed both v^B and v^S to be spin dependent. It will be seen that it is neither necessary nor sufficient to require $v_+\neq v_-$ in order to describe both GMR and GMTP effects. If spin-wave excitations are included, the spin-$\uparrow$ and -$\downarrow$ states are admixed; however, the cross section for such processes is very small at low temperatures.[9,18] Spin-flip scattering through the spin-orbit interaction is also unlikely because of the quenching of orbital angular momentum in transition metals.

By introducing the spinor transformation[19]

$$U=\begin{bmatrix}e^{i(\alpha_p+\gamma_p)/2}\cos\beta_p/2 & e^{i(\alpha_p-\gamma_p)/2}\sin\beta_p/2\\ -e^{-i(\alpha_p-\gamma_p)/2}\sin\beta_p/2 & e^{-i(\alpha_p+\gamma_p)/2}\cos\beta_p/2\end{bmatrix} \tag{3}$$

to transform electron states onto the $x'y'z'$ frame, we apply the Born approximation to Eq. (1) and obtain

$$\rho_\uparrow^p=\frac{\mu}{ne^2}\frac{1}{\tau_\uparrow^p}=\frac{\nu_p}{\nu}\cos^2\frac{\beta_p}{2}(\rho_+^{(s)}+\rho_+^{(d)})+\frac{\nu_p}{\nu}\sin^2\frac{\beta_p}{2}(\rho_-^{(s)}+\rho_-^{(d)})\,, \tag{4}$$

$$\rho_\downarrow^p=\frac{\mu}{ne^2}\frac{1}{\tau_\downarrow^p}=\frac{\nu_p}{\nu}\sin^2\frac{\beta_p}{2}(\rho_+^{(s)}+\rho_+^{(d)})+\frac{\nu_p}{\nu}\cos^2\frac{\beta_p}{2}(\rho_-^{(s)}+\rho_-^{(d)})\,, \tag{5}$$

where μ is the effective mass of s electrons, n is the density of spin-$\uparrow$ or -$\downarrow$ electrons, and

$$\rho_\delta^{(s)}=\frac{\mu}{ne^2}\frac{N^{(s)}(E_F)}{2\hbar}\int d\Omega\left[1-\frac{\mathbf{k}\cdot\mathbf{k}'}{k^2}\right]\left[n_B|v_\delta^B(\mathbf{k}'s,\mathbf{k}s)|^2+\frac{a_p}{\nu_p}n_S|v_\delta^S(\mathbf{k}'s,\mathbf{k}s)|^2\right]\quad(\delta=+,-)\,, \tag{6}$$

$$\rho_\delta^{(d)}=\frac{\mu}{ne^2}\frac{N_\delta^{(d)}(E_F)}{2\hbar}\int d\Omega\left[n_B|v_\delta^B(\mathbf{k}'d,\mathbf{k}s)|^2+\frac{a_p}{\nu_p}n_S|v_\delta^S(\mathbf{k}'d,\mathbf{k}s)|^2\right]\quad(\delta=+,-)\,, \tag{7}$$

Here ν_p and a_p are the volume and surface area of the pth granule, ν is the volume of the sample, $v_\delta(\mathbf{k}'l,\mathbf{k}s)=\int\Psi_{\mathbf{k}'l}^*v_\delta\Psi_{\mathbf{k}s}d\mathbf{r}$, $\Psi_{\mathbf{k}s}$ and $\Psi_{\mathbf{k}'l}$ are the spatial parts of electron wave functions, $N^{(s)}(E_F)$ and $N_\delta^{(d)}(E_F)$ are the DOS of s- and d-electrons at the Fermi surface with spins along $(\delta=+)$ and opposite $(\delta=-)$ to $\mathbf{m}_p$, and n_B and n_S are the bulk and interfacial impurity density of the individual grain. Note that for transition metals $N_+^{(d)}(E_F)\neq N_-^{(d)}(E_F)$ due to the influence of the exchange field, as is shown schematically in Fig. 1.

From Eqs. (4) and (5) we see that $1/\tau_\sigma^p$ varies from one grain to another due to the change of β_p. Assuming the mean-free path to be much larger than the particle sizes and their separations, we can write the resistivity of each channel as $\rho_\sigma=(1-\eta)\rho_0+\sum_p\rho_\sigma^p$, where $(1-\eta)\rho_0$ is the contribution from impurity scattering in the nonmagnetic matrix, $\eta=\sum_p\nu_p/\nu$ is the volume fraction of the magnetic particles, and the summation runs over the whole sample. This gives

$$\rho_\uparrow=\rho_{\rm sym}+\rho_{\rm asy}\left[\frac{M}{M_s}\right], \tag{8}$$

$$\rho_\downarrow=\rho_{\rm sym}-\rho_{\rm asy}\left[\frac{M}{M_s}\right], \tag{9}$$

where

$$\rho_{\rm sym}=\left[(1-\eta)\rho_0+\frac{\eta}{2}(\rho_+^{(s)}+\rho_-^{(s)}+\rho_+^{(d)}+\rho_-^{(d)})\right]$$

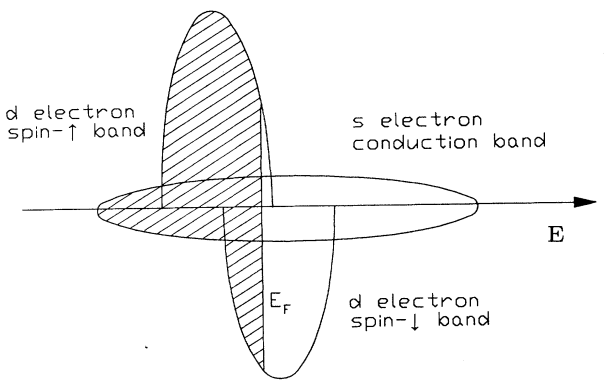

FIG. 1. A schematic diagram of the density of states of s and d bands in transition metals.

and

$$\rho_{\text{asy}}=\frac{\eta}{2}(\rho_{+}^{(s)}-\rho_{-}^{(s)}-\rho_{+}^{(d)}-\rho_{+}^{(d)})$$

are the symmetric and asymmetric parts of resistivity, respectively, $M=(\sum_p m_p\cos\beta_p)/\nu$ is the global magnetization, $M_s=\sum_p m_p/\nu$ is the saturation magnetization, $m_p=\nu_p M_b$, and M_b is the bulk magnetization of the magnetic grains. We emphasize that η and M/M_s are geometric factors determined only by $\{\nu_p\}$ and $\{\beta_p\}$. The assumption of a long mean-free path (compared with the particle sizes and their separations) permits the use of global average here. It is interesting to note that $\rho_\uparrow$ and $\rho_\downarrow$ change linearly with (M/M_s) in opposite directions. At zero field, because of the random orientations of the magnetic particles, all electrons experience identical scattering and $\rho_\downarrow=\rho_\uparrow$. The scattering becomes asymmetric for two different electron spins when $H\neq 0$. As H increases, one branch becomes more conductive while the other becomes more resistive. When $H\geq H_s$, $M/M_s=1$ and the $\rho_\uparrow$ and $\rho_\downarrow$ reach their maximum asymmetry.

In the two-current model[18] the two spin channels conduct in parallel so that $\rho=\rho_\uparrow\rho_\downarrow/(\rho_\uparrow+\rho_\downarrow)$. From Eqs. (8) and (9), we obtain the resistivity and the MR:

$$\rho=\frac{1}{2}\rho_{\text{sym}}\left[1-\left[\frac{\rho_{\text{asy}}}{\rho_{\text{sym}}}\right]^2\left[\frac{M}{M_s}\right]^2\right], \tag{10}$$

$$\frac{\rho(H)-\rho(0)}{\rho(0)}=-\left[\frac{\rho_{\text{asy}}}{\rho_{\text{sym}}}\right]^2\left[\frac{M}{M_s}\right]^2. \tag{11}$$

The field dependence of the MR is fully contained in geometric factors $(M/M_s)^2$ through the change of $\{\beta_p\}$, whereas dynamics is included in ρ_{sym} and ρ_{asy}. Considering that the maximum GMR observed in experiments is 43%,[7] and using Eqs. (8), (9), and (11), we estimate the maximum asymmetry (corresponding to $H\geq H_s$ or $M/M_s=1$) of scattering to be $\rho_\uparrow/\rho_\downarrow\approx 5$ (or $\rho_\downarrow/\rho_\uparrow\approx 5$ if $\rho_{\text{asy}}<0$). This is a typical number found in experimental studies of various transition metal based alloys,[18] and is also consistent with an estimation from DOS data of transition metals. It is worth emphasizing that the MR in Eq. (11) is proportional to $(M/M_s)^2$, which agrees with experimental measurements reported in Ref. 7.

As can be seen from Eqs. (10) and (11) and the definitions of ρ_{sym} and ρ_{asy}, the GMR has two sources: the spin-dependent scattering potential and the spin-dependent DOS of the d bands. When $v_+\neq v_-$ and in the absence of unfilled d bands, we have $\rho_\delta^{(d)}=0$ and $\rho_{\text{asy}}=\rho_+^{(s)}-\rho_-^{(s)}$; s-s scattering alone gives rise to a negative MR. This is essentially the mechanism proposed in Refs. 8 and 9. In the second case, where $v_+=v_-$ and $\rho_-^{(s)}=\rho_+^{(s)}$, GMR arises from asymmetric s-d scattering because $N_+^{(d)}(E_F)\neq N_-^{(d)}(E_F)$. While both mechanisms offer an equally good explanation of the GMR effect, we point out that there are other experimental features which cannot be accounted for by the s-s scattering mechanism alone. For instance, GMR and related magnetotransport properties appear to be unique to systems containing transition metals. Despite many attempts, no evidence of negative GMR has been reported in rare-earth–nonmagnetic metal structures.[7,12,13] In rare-earth metals, the $4f$ orbits that give rise to the magnetism are highly localized and there is little difference in spin-↑ and -↓ DOS at E_F. The failure to observe negative GMR in rare-earth systems strongly implicates the importance of the unfilled d bands of the transition metal constituent.

Experimentally, very large magnetothermopower (MTP) effects correlated with MR have been observed in multilayers,[14,15] and most recently, in granular solids.[16] MTP depends sensitively on the electronic band structure, and thus provides a crucial test of any electronic transport theory.[20] We calculate the MTP of the granular systems by using the usual relation $S=(\pi^2k_B^2T/3e)(\partial\ln\rho/\partial E)$ and Eq. (10), and obtain

$$S(H)=A\frac{\rho(0)}{\rho(H)}+C\ . \tag{12}$$

The quantities

$$A=\frac{2\pi^2k_B^2T}{3e}\left[\frac{\partial\ln\rho_{\text{sym}}}{\partial E}-\frac{\partial\ln\rho_{\text{asy}}}{\partial E}\right]$$

and

$$C=\frac{2\pi^2k_B^2T}{3e}\left[\frac{\partial\ln\rho_{\text{asy}}}{\partial E}-\frac{1}{2}\frac{\partial\ln\rho_{\text{sym}}}{\partial E}\right]$$

are independent of H. The field dependence of the thermopower enters only through $\rho(H)$. For the ordinary s-s scattering model with no unfilled d bands and with spin-dependent interactions (i.e., $v_+\neq v_-$) and the same final density of states $N^{(s)}$ for both spins throughout the sample,[9] we have

$$\frac{\partial\ln\rho_{\text{sym}}}{\partial E}=\frac{\partial\ln\rho_{\text{asy}}}{\partial E}=\frac{n}{N^{(s)}}\frac{\partial}{\partial E}\left[\frac{N^{(s)}}{n}\right]$$

due to

$$\frac{\partial\rho_\delta^{(s)}}{\partial E}=\rho_\delta^{(s)}\frac{n}{N^{(s)}}\frac{\partial}{\partial E}\left[\frac{N^{(s)}}{n}\right]\quad(\delta=+,-)$$

and

$$\frac{\partial\rho_0}{\partial E}=\rho_0\frac{n}{N^{(s)}}\frac{\partial}{\partial E}\left[\frac{N^{(s)}}{n}\right].$$

Thus one finds $A\equiv 0$, and $[S(H)-S(0)]/S(0)\equiv 0$ at any field H, indicating that the s-s scattering mechanism is unable to explain the experimentally observed GMTP and its strong correlation with GMR without involving other mechanisms.[21] On the other hand, in our model the MTP and its correlation with $\rho(H)$ arise naturally as a result of unfilled d bands. In the presence of unfilled d bands, $A\neq 0$, and $S(H)$ is inversely proportional to $\rho(H)$. The s-d scattering should therefore be an essential ingredient of the GMR and GMTP effects. This result provides additional strong support for our argument that the s-d scattering due to $N_+^{(d)}(E_F)\neq N_-^{(d)}(E_F)$ rather than s-s scattering due to $v_+\neq v_-$ is the main contributor to the novel magnetotransport in these systems. It should be stressed that the above argument that $A\equiv 0$ for s-s

scattering is made under the assumption that the energy dependence of resistivity comes mainly from the density of states effects. A fine-tuning of the impurity potential (e.g., via resonant scattering) might allow for a modeling of magnetothermopower without s-d scattering but this is entirely unnatural in our view.

It is worth noting that our theoretical prediction of $1/\rho(H)$ scaling behavior of the MTP and its linear temperature dependence in the granular solids have been observed recently.[16] The interesting scaling is a direct consequence of interplay between magnetism and electronic transport in the system.

At fixed volume fraction, the GMR has been found to depend on particle size;[7,22] it is optimized when the sizes are of the order of electron mean-free path λ. Physically, this is understandable. When the size of grains and their separations are smaller than λ, an electron sees different magnetic granules, and the relaxation rate is an average of the contributions from each grain, i.e., Matthiessen's rule holds. When the sizes are much larger than λ, however, intraparticle scattering dominates the physics. In the limiting case, the system behaves like a bulk ferromagnetic material and the GMR vanishes. On the other hand, grain sizes should not be so small as to greatly enhance $\rho(0)$ by increasing interfacial area, or even to seriously modify the electronic structure of the ferromagnetic particles. Thus an optimal size for GMR is to be expected. Unfortunately, the size dependence cannot be addressed in our treatment. When the sizes become larger than λ, our approach breaks down, and a random-resistor-network type of model becomes relevant.[23]

In summary, we have presented a new framework for dealing with magnetotransport in magnetic granular solids and multilayers. We have shown that the ordinary s-s scattering mechanism proposed in Refs. 8 and 9 *cannot* explain the experimentally observed GMTP and its strong correlation with the GMR effect, as well as the null GMR results of rare-earth-nonmagnetic structures. Furthermore, we have demonstrated that both the remarkable GMR and GMTP effects arise naturally from spin-dependent s-d scattering rates due to the different DOS for majority and minority d band of the magnetic component. In the present formulation we are able to treat GMR and GMTP effects on an equal footing, and to provide *explicit* expressions of the GMR and GMTP for magnetic granular solids. These formulas relate GMR and GMTP to microscopic and geometric quantities, and are in accordance with the experimental results.

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[23]Lei Xing, D. M. Frenkel, and Y. C. Chang (unpublished); for a recent review of random-resistor network, refer to D. Bergman and D. Stroud, *Solid State Physics* edited by H. Ehrenreich and D. Turnbull (Academic, Boston, 1992), Vol. 46, p. 147. The crossover from the case of small particles, which is studied in this paper, to the random-resistor network deserves further study.