First Order Magnetization Process in Polycrystalline Perovskite Manganite

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The Ising spin model with random competing ferromagnetic, antiferromagnetic exchange interactions in the external field is used to investigate the First Order Magnetization Process at low temperature in doped polycrystalline magnetic perovskite Pr$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$M$_x$O$_3$ (M = Co, Ga). Using Callen identity in the correlated effective field approximation, our calculation describes well the experimental behavior, which is explained by the reorientation of antiferromagnetic clusters and by the expansion of ferromagnetic clusters in the external field at low temperature. The origin of the number of critical fields at which the steps of magnetization occurred, the magnitude of these steps and the related jumps in the magnetic field dependent resistivity are also discussed.

1. Introduction

First order magnetization process (FOMP) or magnetic field –induced metamagnetic transition at low temperature is a well-known phenomenon occurred in crystalline antiferromagnets, (see Ref. 1)). A new kind of FOMP is also observed experimentally in polycrystalline substituted magnetic perovskites, (see Ref. 1)). A new kind of FOMP is also observed experimentally in polycrystalline substituted magnetic perovskites, (see Ref. 1)). Two main magnetic competing interactions, anti-ferromagnetic (AF) super-exchange between the same valence manganese ions (Mn$^{3+}$-Mn$^{3+}$, Mn$^{4±}$-Mn$^{4±}$) and ferromagnetic (FM) double exchange interactions between Mn$^{4±}$-Mn$^{4±}$ ions, are responsible for the formation of the AF and FM clusters. In the presence of an external magnetic field, competition between these two types of clusters determines behaviors of magnetization process as well as the FOMP. From the simplest theoretical point of view, magnetic properties of these systems can be examined by considering the Ising spin system with random AF and FM exchange interactions. The FOMP theory was intentionally developed in the square Ising spin lattice with random AF, FM nearest neighbor (NN) exchange interactions and also applied to explain the re-entrant magnetism phenomenon in perovskites. This paper is aimed to employ this method to examine the FOMP and to extend this theory to describe the magneto-resistance anomaly in the bulk Pr$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$M$_x$O$_3$ (M = Co, Ga) polycrystalline perovskites.

2. Background of Phenomenological Theory

Details of FOMP in square random exchange spin lattice are developed. Here we briefly review and extend it to describe magnetoresistance. Hamiltonian for the Ising spin system with random AF and FM NN interaction has the following form

\[ H = - \frac{1}{2} \sum_{j \neq k} J_{jk} S_j S_k - g \mu_B h_c \sum_j S_j \] (1)

with $S_j$ a spin variable at site $j$ having two values $S_j = \pm S$. $J_{jk}$ is the NN exchange integral, which can be considered as a random variable subject to the following distribution law

\[ P(J_{jk}) = p \delta[J_{jk} - J_{FM}] + (1 - p) \delta[J_{jk} - J_{AF}] \] (2)

Here $J_{FM} = J(1 + \Delta)$, $J_{AF} = J(1 - \Delta)$ are mean values of the FM (AF) interaction strength, respectively. $\Delta$ is a fluctuation quantity characterizing for the deviation of the exchange strength from its average value $J$ ($\Delta > 1$) and $h_c$ is the external magnetic field. Using an integral transformation for Callen identities and the NN correlated effective field approximation, we can obtain following equations for the relative magnetization per site

\[ m = \langle (S_j) \rangle_T / S \]

\[ m = \sum_{n=0}^{\infty} C_n \alpha^n \sinh(\beta h_c) \] (3)

where double brackets imply taking the thermodynamic and the random averages. $C_n$ is a binomial coefficient and $z$ is the NN spin number.

\[ A_n = \int_0^\infty \frac{a^{z-n}(x)b^n(x)}{\sinh(\beta h_c/2)} \sin[(ah + n\pi/2)dx] \]

\[ a(x) = p \cos \alpha(1 + \Delta)x + (1 - p) \cos \alpha(1 - \Delta)x \]

\[ b(x) = p \sin \alpha(1 + \Delta)x + (1 - p) \sin \alpha(1 - \Delta)x \] (4)

In the formula (3)-(4), the following dimensionless quantities are noted as $\tau = k_B T / J$, $\alpha = \gamma^{-1}$, $h = g\mu_B h_c / J$. Equation for Curie temperature $T_C$ is easily obtained from eq. (3) as the solution of equation $1 - z A_1(\alpha, p, \Delta, h) = 0$ with $\alpha_c = J/k_B T_C$. The following theoretical parameters will determine the magnetization process: $z$ - the number of NN spins depending on types of spin lattice, $\Delta$ - the relative fluctuating quantity of AF, FM exchange interactions, $h$ - the reduced external magnetic field, $\alpha$ inverse temperature parameter, $p$ and (1-$p$) probabilities of having FM and AF NN exchanges depending on the amounts of three (Mn$^{3+}$) and four valence (Mn$^{4±}$) manganese ions.

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Magnetoresistance in polycrystalline perovskites at low field can be explained by the granular tunneling magnetoresistance concept\(^{8,9}\) combining with the fluctuating magnetization approach which has been mentioned above. According to the theory of granular tunneling magnetoresistance,\(^{10}\) the relative resistivity of granular media in the external field is estimated qualitatively by:

\[
\frac{\rho(h, \tau)}{\rho_0(\tau)} = \frac{1}{1 + P^2 m^2}
\]

where \(P\) is conducting electron polarization. In each FM conducting cluster, itinerant electron spins are strongly polarized along the localized spin direction due to large local Hund interaction \(J_{fi}\). Electron polarization is mostly saturated, which is estimated by:

\[
P = \frac{n_+ - n_-}{n_1 + n_-} = \tanh \left[ \frac{J_{hi}}{\tau} \left( S + \frac{1}{2} \right) \right]
\]

where \(J_{hi}\) is \(J_{fi}/J\). It is clearly seen that at a given temperature, the resistance decreases with increasing magnetization. Step-up change in the magnetisation while increasing field will bring about the step-down change in the field dependent resistance.

3. Calculation and Comparison with Experiment

In this part we calculate magnetic and resistance characteristics using formulas in Sect. 2. Figures 1, 2, 5 have general meaning, which are plotted using dimensionless quantities. Other curves in Figs. 3, 4 are shown for the purpose of comparing with experimental measurements.

Figure 1 shows the thermomagnetic plots for a square spin lattice at different low external field strength \(h\) with \(z = 4\), \(p = 0.5\), \(\Delta = 1.02\). We can see that two Curie temperatures, the low \((T_{c1})\) and the high \((T_{c2})\) one, exist in an extremely low magnetic field, which is named reentrant magnetism (RM\(^{10}\)). When the magnetic field gradually increases, the low Curie temperature is blurred due to the shrinking AF clusters until it absolutely vanishes. Only high Curie temperature \(T_{c2}\) is left and is approximated by the intersection between the steepest slope of the thermomagnetic curve and the temperature axis. It is clearly seen that the expansion of FM clusters and the shrinking of AF clusters in the higher field imply an increase of magnetization and the higher \(T_{c2}\).

Figure 2 presents a dependence of Curie temperature on probability \(p\) of FM exchange interaction for square spin lattice with \(z = 4\), \(\Delta = 1.15\) at zero and different strong external field \(h\). At zero field, the RM phenomenon only occurs at FM interaction probability \(p\) larger than some critical value \(p_{c1}\) (see curve with \(h = 0\)) since the system is disordered when \(p < p_{c1}\) (the percolation threshold). With \(p > p_{c1}\), FM clusters are formed among AF clusters, which is required for occurring RM. In the presence of high fields, this condition is only assured when \(p\) is limited within a certain interval. The upper critical probability existence means that at \(p > p_{c2}\) ferromagnetic clusters are totally dominated in the high field, thus there is only one high Curie temperature \(T_{c2}\).

Figure 3 illustrates the comparison between theoretical and experimental FOMP curves observed in Pr\(_{0.5}\)Ca\(_{0.5}\)Mn\(_{0.95}\)-Co\(_{0.05}\)O\(_3\) (see Ref. 2)). Parameters of the theoretical curve are chosen as \(z = 4\), \(\Delta = 1.04\), \(\Delta = 1.04\), \(S = 1\). We can see that two jumps of magnetization at two critical fields are well reproduced in theoretical curve and its magnitudes are given in Table 1.

The theoretical and experimental curves\(^{4}\) are shown in Fig. 4 for FOMP of Pr\(_{0.5}\)Ca\(_{0.5}\)Mn\(_{0.97}\)Ga\(_{0.03}\)O\(_{3.5}\). Parameters
for the theoretical curve are chosen as \( z = 6, p = 0.5, \Delta = 1.04, S = 1 \). The magnitude of the magnetization steps at three critical fields are also evaluated and listed in Table 2. These theoretical and experimental values for the second and the third critical fields reasonably agree, except for the first one in the low field region. The domain displacement is probably dominated in the low field polycrystalline magnetization process, hence it is not properly described by the microscopic Ising model.

The number of critical fields in Figs. 3 (4) is 2 (3) at a given measure of fluctuation \( \Delta = 1.04 \) mainly depends on the probability of AF interaction \((1-p)\) and the number of NN spins \((z = 4\) and 6 for these figures). The Probability \((1-p)\) defines the available percentage of spins among \( z \) neighbors, which can be reoriented in presence of the external field. For example, when \( z = 6 \), and probabilities of AF, FM interactions are the same \( p = 0.5 \) (Fig. 4), three NN spins may be reversed corresponding to three magnetization steps observed. The magnitude of steps depends on the spin value \( S \), the measure of fluctuation \( \Delta \) and the number of AF clusters that becomes smaller with increasing field. It is the reason why the magnitude of magnetization steps in the high field region is smaller than its step in the low field region.

In Fig. 5 we show the calculated relative resistivity as a function of magnetic field with the same parameters given in Fig. 3. Step-down change of relative resistivity at two critical fields corresponds to step-up change of the magnetization shown in Fig. 3.

### 4. Conclusion

Ising spin model with fluctuating competing AF, FM exchanges is used for explaining FOMP and the related steps in the field dependence of resistivity observed in doped perovskite manganite \( \text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Co}_{x}\text{Ga}_{x} \). The number of FOMP steps and its magnitude depend mostly on the type of spin lattice (via NN spin numbers \( z \)), spin value \( S \), the probability of AF bonds \((1-p)\), and the fluctuation quantity \( \Delta \). The calculation results for the FOMP steps and its magnitude are well compared with experimental data.

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