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The effect of the itinerant spin-polarized carriers on magnetization in double-perovskite ferrimagnet $\text{Sr}_2\text{FeMoO}_6$

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Abstract

Recent experiments have shown that ordered half-metallic $\text{Sr}_2\text{FeMoO}_6$ exhibits a net moment of less than $4 \mu_B$. In disordered $\text{Sr}_2\text{FeMoO}_6$, the linear correlation between saturated magnetization and antisite defect concentration disagrees with the prediction of published models. In this paper, we propose a model which considers both contributions of ferromagnetic interaction (double-exchange mechanism) induced by itinerant spin-polarized carriers and antiferromagnetic interaction. Both in ordered and in disordered $\text{Sr}_2\text{FeMoO}_6$, the saturated magnetization is studied. It is found that the itinerant polarized carriers have a large effect on the saturated magnetization. Our calculation results explain experimental results very well.

1. Introduction

The colossal magnetoresistance (CMR), a substantial reduction of electrical resistance near the Curie temperature T_C in the presence of applied magnetic field, is observed in single-crystal manganite and epitaxial manganite films [1]. But this extraordinary magnetoresistance is difficult to apply in electronic devices due to its narrow range of temperature and high applied magnetic field. Recently, it has been reported that the double perovskite $\text{Sr}_2\text{FeMoO}_6$ exhibits a significant magnetoresistance (MR) at 300 K under a magnetic field $H < 2$ kOe [2]. This special property could not be found in perovskite manganite. The double-perovskite structure compound has a crystal structure of $\text{Sr}_2\text{BB}'\text{O}_6$, where B and B' sites are occupied alternately by ordered transition-metal ions Fe^{3+} ($3d^5$; $t_{2g}^3 e_g^2$, $S = 5/2$) and Mo^{5+} ($4d^1$; t_{2g}^1 , $S = 1/2$) [3, 4]. The experimental results of the optical conductivity spectrum indicate $\text{Sr}_2\text{FeMoO}_6$ has a half-metallic electronic structure [5]. The majority-spin band presents a gap and the

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corresponding $3d^5$ up-spin electrons are localized in the Fe^{3+} ion, while the conduction band is partially occupied by the $4d^1$ down-spin electrons of Mo^{5+} ions. Furthermore, the observed magnetic transition temperature for Sr_2FeMoO_6 is as high as 410–450 K [6, 7]. Due to its high ferromagnetic transition temperature and half-metallic structure, the unusually high spin polarization of conduction electrons (>60%) can be found even around room temperature. These properties may lead to the large low field magnetoresistance (LFMR) at room temperature. As a result, because of the significant room temperature LFMR, Sr_2FeMoO_6 could be proposed as a better candidate material to be used in spintronics than perovskite manganite.

Previous measurements of magnetization in ordered Sr_2FeMoO_6 showed a net moment of $\sim 3-3.4 \mu_B$ at 4.2 K [4, 8]. Firstly, these measured results implied an antiferromagnetic coupling between the Fe and Mo moments ($5 - 1 = 4 \mu_B$). Otherwise a ferromagnetic coupling would lead to a larger net moment ($5 + 1 = 6 \mu_B$). Furthermore, it was found that even in ordered Sr_2FeMoO_6 the net moment was always less than $4 \mu_B$. So far, explanations of this problem have not been reported in the literature. In addition, we can also find the concentration A_s of the antisite defects (A_s is concentration of Fe ions at the Mo sites) will decrease the saturated magnetization M_s of Sr_2FeMoO_6 . A linear formula $M_s = a + b \times A_s$ (a and b are fitting parameters) is often used to describe the dependence of the saturated magnetization on the Fe–Mo disorder. The Monte Carlo computation of Ogale *et al* [9] has predicted that $M_s = (4 - 8 \times A_s) \mu_B$ and $T_c = (456 - 300 \times A_s)$ K. Alternatively, it is proposed that if one assumes the local superexchange rules for $3d^5-3d^5$, $4d^1-4d^1$ and $3d^5-4d^1$ hold at the antisite, $M_s = (4 - 10 \times A_s) \mu_B$ will be obtained [5]. In detail, if a Mo^{5+} ($S = 1/2$) is at the B (Fe) site surrounded by the Mo^{5+} neighbours, its magnetic moment tends to be parallel to those of the Mo^{5+} ions, which decreases the net magnetization by $6 \mu_B$. Inversely, if an Fe^{3+} ($S = 5/2$) is at a B' (Mo) site, its magnetic moment tends to be antiparallel to those of the Fe^{3+} ions, causing a decrease in net magnetization by $4 \mu_B$. Therefore the total decrease in magnetization per pair of the antisite defects is as large as $10 \mu_B$ [5]. But the experimental result [10] ($M_s = (3.62 - 3.3 \times A_s) \mu_B$) still could not be explained by all these presented models.

Suppose this ordered compound is not an insulator yet, but a metal. Therefore, the electronic itinerancy of minority-spin electrons must be taken into account in the magnetic interaction.

The aim of this paper is to present a rationalized explanation of the net moment less than $4 \mu_B$ in ordered Sr_2FeMoO_6 and the correlation $M_s = (3.62 - 3.3 \times A_s) \mu_B$ in disordered Sr_2FeMoO_6 based on considering the influence of the itinerant carriers on the saturated magnetization. In such a case, it has been often suggested [11–13] that the ferromagnetic coupling of the Fe ions can be described as a sort of double-exchange mechanism as proposed by Zener [14] involving $Fe^{3+}-O-Mo-O-Fe^{2+}$ charge transfer. A mean field approximation (MFA) [15, 16] is applied to ferrimagnetic Sr_2FeMoO_6 with two sublattices. Both the antiferromagnetic interaction between the two sublattices and the double-exchange (DE) interaction induced by itinerant carriers are taken into account. We also study the variation of the Curie temperature with the concentration of antisite disorder.

2. Model

2.1. Ordered system

Band structure results suggested that the B and B' sites in this ordered compound consist of Fe^{3+} and Mo^{5+} ions alternating along the cubic axes. Therefore the B and B' sites could

be divided into two sublattices, i.e. Fe and Mo sublattices. There is an anti-ferromagnetic coupling between sublattices. In particular, it is assumed that the itinerant spin-polarized charge carriers exist in one of the sublattices, namely the Fe sublattice, designated as B in Sr₂FeMoO₆. Correspondingly, the Mo sublattice will be designated as B' in Sr₂FeMoO₆.

The MFA could be carried out to simplify the ferrimagnetic coupling between sublattice B (Fe) and B' (Mo). The inter-sublattice interaction will be represented by means of the effective field. The effective fields in sublattices B and B' are proportional to the thermal mean values of the spin *z* components in sublattices at equilibrium respectively.

$$m_B = \langle S_B^Z \rangle_{\text{eq}}; \quad m_{B'} = \langle S_{B'}^Z \rangle_{\text{eq}}.$$

When the effective field m_B in the B (Fe) sublattice is fixed, the equilibrium value of $m_{B'}$ in the B' (Mo) sublattice is expressed by the well known equation of the mean field theory.

$$m_{B'} = S' B_{S'}[\lambda_{B'B} m_B + \lambda_{B'B'} m_{B'}]. \quad (1)$$

Here, $B_{S'}$ denotes the Brillouin function and the coefficient $\lambda_{B'B}$ is defined as

$$\lambda_{B'B} = \beta S' J_{B'B} Z_B(B') \quad (2)$$

where $Z_B(B')$ represents the number of nearest-neighbour B ions to the B' ion. $J_{B'B}$ indicates the antiferromagnetic coupling strength between B and B' ions, and $\beta = 1/k_B T$.

Therefore $\lambda_{B'B}$ could be rewritten as

$$\lambda_{B'B} = 3\beta J_{B'B}. \quad (3)$$

Similarly $\lambda_{B'B'}$ could be defined as

$$\begin{aligned} \lambda_{B'B'} &= \beta S' J_{B'B'} Z_{B'}(B') \\ &= 6\beta J_{B'B'} \end{aligned} \quad (4)$$

where $Z_{B'}(B')$ represents the number of nearest-neighbour B' ions to the B' ions. $J_{B'B'}$ indicates the antiferromagnetic coupling strength between B' and B' ions.

When the equilibrium value of $m_{B'}(\text{eq})$ is fixed, the equilibrium value of the spin *z* component per ion in the B (Fe) sublattice will be obtained by the treatment of Kubo and Ohata [15]. The effective field H_{eff}^Z that determines the orientations of the spin in the B (Fe) sublattice is included in the MFA parameter λ .

$$\lambda = \beta S g \mu_B H_{\text{eff}}^Z. \quad (5)$$

Therefore, when the concentration of the itinerant carriers is x in the B sublattice, the mean value of the spin is given by

$$m_B(\lambda) = \langle S_B^Z(\lambda) \rangle = (1-x) S B_S(\lambda) + x S'' B_{S'}\left(\frac{S''}{S} \lambda\right) \quad (6)$$

where S'' is a total spin composed of a spin $S(\text{Fe})$ and an itinerant carrier $\sigma = 1/2$ according to the Hund rule ($S = 5/2$ and $S'' = 2$ for Sr₂FeMoO₆).

The value of the equilibrium MFA parameter λ or m_B could be deduced from the extremum free energy of the B (Fe) sublattice system which consists of the itinerant electrons and localized spins. By use of the mean field approximation, the free energy per ion in the B sublattice is denoted as

$$f_B = x\mu + \Omega + \langle H_E \rangle - T S^{(S)} \quad (7)$$

where μ means the chemical potential and Ω is the grand-canonical potential of itinerant carriers. $\langle H_E \rangle$ represents the contribution to the energy which arises from the effective field from sublattice B' and the ferromagnetic exchange interaction inside sublattice B,

$$\langle H_E \rangle = -\frac{1}{\beta S} \left[m_B \lambda_{BB'} m_{B'} + \frac{1}{2} \lambda_{BB} m_B^2 \right] \quad (8)$$

and $S^{(S)}$ indicates the entropy when the ion spins S , S' are randomly distributed in the B sublattice. To obtain the equilibrium value of λ or m_B , equation (7) should be minimized at fixed m_A .

The term $(x\mu + \Omega)$ in equation (7) means the temperature-dependent free energy of carriers. We assumed that it could be replaced by the temperature-independent mean energy. According to [15], the temperature-independent mean energy is equal to $\gamma_s(\lambda)\varepsilon$, where ε is the mean 'bare' band energy at $T = 0$ K and the DE band-narrowing factor $\gamma_s(\lambda)$ is given by

$$\gamma_s(\lambda) = \frac{1}{2} + \frac{S}{2S+1} \coth\left(\frac{2S+1}{2S}\lambda\right) \left[\coth(\lambda) - \frac{1}{2S} \coth\left(\frac{\lambda}{2S}\right) \right]. \quad (9)$$

Consequently, the minimum condition of f_B in equation (7) is written as

$$\beta S \varepsilon \frac{\partial \gamma_s}{\partial m_B} - (\lambda_{BB'} m_{B'} + \lambda_{BB} m_B) + \lambda = 0. \quad (10)$$

By solving equation (10), together with equations (1) and (6), the equilibrium values of the spin z component of sublattices B (Fe) and B' (Mo) could be obtained respectively. The magnetization of $\text{Sr}_2\text{FeMoO}_6$ is proportional to $m_B - m_{B'}$.

2.2. Disordered system

In our calculations the single disorder is an antisite defect. That is to say, Fe atoms are able to occupy sites in the Mo sublattice (and vice versa) randomly. The alternating ordering of Fe and Mo leads to the existence of pairs of Fe (Mo) ions occupying nearest neighbour sites. This implies the existence of Mo–O–Mo (paramagnetic, PM) and Fe–O–Fe (antiferromagnetic, AF) patches. The existence of AF patches has been firmly established by Mossbauer spectroscopy and the PM Mo–O–Mo patches are to a much lesser extent [17]. Therefore, these will modify our model from two aspects.

- (1) The large Neel temperature [18] implies a strong antiferromagnetic superexchange coupling among Fe–O–Fe patches. Consequently, antisite defects will enhance antiferromagnetic exchange coupling between B and B' sublattices.
- (2) Considering the existence of Mo ions in the Fe sublattice, the effective field of the B sublattice will be revised. When the concentration of the itinerant carriers is x and antisite disorder y in the B sublattice respectively, the magnetization of the B sublattice is given by

$$m_B(\lambda) = \langle S_B^Z(\lambda) \rangle = (1-y)(1-x)S B_S(\lambda) + (1-y)x S' B_{S'}\left(\frac{S'}{S}\lambda\right) + y S'' B_{S''}\left(\frac{S''}{S}\lambda\right) \quad (11)$$

where S'' is a total spin composed of a spin S (Fe) and an itinerant carrier $\sigma = 1/2$ according to the Hund rule ($S = 5/2$ and $S'' = 2$ for $\text{Sr}_2\text{FeMoO}_6$).

2.3. Model parameters

Our model is defined by these parameters: $J_{BB'}$, $J_{B'B}$, J_{BB} , $J_{B'B'}$ and ε . Both $J_{BB'}$ and $J_{B'B}$ represent the anti-ferromagnetic coupling strength between sublattices B and B'. Therefore it can be obtained that $J_{BB'} = J_{B'B}$ and only four parameters are left. In an ordered system, the phase diagram of $\text{Sr}_2\text{FeMoO}_6$ in the ground state has shown that the nearest exchange constant of Fe spins $J_{BB} = 0.03\text{--}0.08$ meV [19]. In this case, we selected the value of J_{BB} as 0.05 meV. For $J_{BB'}$, the estimated values reported in the literature suggest $J_{BB'}/2 = -4.1$ meV [5] or 41.38 K [9]. However, experimental results show that such parameters will lead to a higher

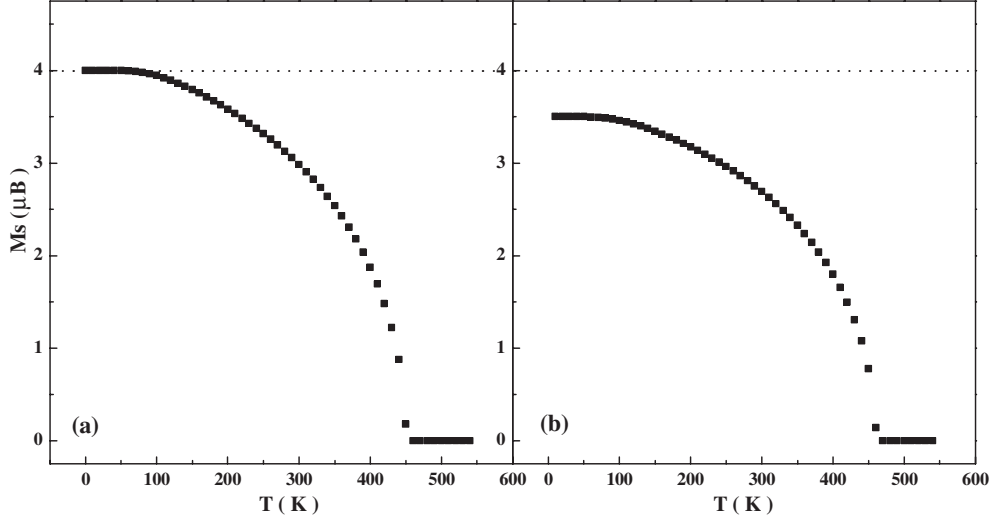


Figure 1. The temperature dependence of the magnetization (a) without and (b) with consideration of the influence of itinerant spin-polarized carriers.

Curie temperature [20]. Therefore, we select the parameter $J_{BB'}/2 = -3.32$ meV. As for $J_{B'B'}$, a compound of the type $\text{RMO}_8\text{O}_{14}$ (R indicates a rare-earth element) shows no magnetic contribution from the Mo ions [20], which suggests a weak magnetic interaction between Mo ions. It is reasonable to assume that $J_{B'B'}$ is close to 0 K. The mean kinetic energy $\langle T \rangle$ of the d electrons in the B sublattice may be estimated by means of the sum rule for the real part of the optical conductivity $\sigma_1(\omega)$ [21],

$$\frac{2}{\pi} \int_0^{\infty} \sigma_1(\omega) d\omega = \frac{N_B e^2}{m^*} \quad (12)$$

where N_B is the number of itinerant carriers and the effective mass m^* is defined by equation (13) [21].

$$\frac{1}{m^*} = -a^2 \frac{\langle T \rangle}{N_B}. \quad (13)$$

m^* is estimated to be ≈ 1.7 [22]. Parameter a is the average lattice constant, $a \approx 0.0395$ nm [22]. Setting $\varepsilon = \langle T \rangle / N_B$, the estimated $\varepsilon = -300$ K is obtained.

3. Results and discussion

To further quantify the contribution of itinerant electrons, the special case without itinerant electrons, namely zero DE interaction, will be first considered. In this case, equation (10) will be degenerated to the following equation.

$$\lambda = \lambda_{BB'} m_{B'} + \lambda_{BB} m_B. \quad (14)$$

Figure 1(a) shows the variation of the magnetization with temperature in this case. Using parameters $-J_{BB'} = J_{B'B} = -67.53$ K, $J_{BB} = 5.28$ K and $J_{B'B'} = 0$ K (no exchange interaction), we could find a full saturated moment of 4 μ_B and a Curie temperature value which is close to the experimentally observed value of 450 K [7].

In figure 1(b), we consider the contribution of itinerant carriers to the saturated magnetization and the Curie temperature. From the experimental results of the Hall resistivity

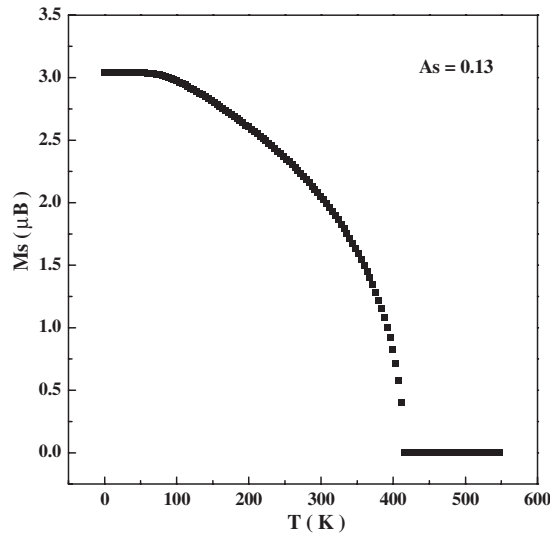


Figure 2. The dependence of the magnetization on temperature for $A_s = 0.13$.

in the $\text{Sr}_2\text{FeMoO}_6$ crystal, it is known that the density of the conduction electrons is estimated at $1.1 \times 10^{22} \text{ cm}^{-3}$, which corresponds to nearly one electron-type carrier per pair of Fe and Mo [5]. Meanwhile, in our model it has been assumed that the itinerant spin-polarized charge carriers only exist in the B (Fe) sublattice. Therefore, it is reasonable to take the concentration of itinerant carriers x as 0.5. As shown in figure 1(b), with the parameter $\varepsilon = -300 \text{ K}$, the saturated magnetization decreases to $3.5 \mu_B$ evidently, but the Curie temperature only increases to 460 K. Seen from our calculation results, the existence of the itinerant carriers will give rise to the decrease of saturated magnetization at the lowest temperature. Even in ordered $\text{Sr}_2\text{FeMoO}_6$ the saturated magnetization will be less than $4 \mu_B$, which is consistent with the experimental results [4, 9].

To compare with the experimental data in [3], we calculate the dependence of the magnetization on the temperature with antisite disorder concentration $A_s = 0.13$. Figure 2 shows the dependence of the magnetization on the temperature in $\text{Sr}_2\text{FeMoO}_6$ with antisite disorder concentration 0.13. The saturated magnetization at the lowest temperature is $3.05 \mu_B$ and the Curie temperature is 416 K, which is very close to the experimental results ($M_s = 3.1 \mu_B$, $T_c = 415 \text{ K}$) [3]. The parameter $-J_{BB'}$ is chosen as 77.5, which is more than the 67.5 used in ordered $\text{Sr}_2\text{FeMoO}_6$. The reason is that Fe-Fe ($3d^5-3d^5$) superexchange interaction will enhance the strength of antiferromagnetic coupling between B and B' sublattices. Our calculation agrees with the experimental results very well. It indicates that our model is appropriate to describe the magnetization of disordered $\text{Sr}_2\text{FeMoO}_6$.

Now, for the sake of establishing universal correlations between the antisite disorder concentration A_s and saturated magnetization M_s , the saturated magnetization at 5 K is plotted as a function of the antisite disorder concentration according to our model (figure 3(a)). Our calculation results reveal that M_s has an almost linear dependence on the antisite concentration A_s ($M_s = a + b \times A_s$, $a = 3.53$, $b = -3.56$). In figure 3(b), we also show the experimental observed dependence of M_s on A_s for a wide set of $\text{Sr}_2\text{FeMoO}_6$, including most of the data reported in the literature. The detailed saturated moments for all samples as well as the antisite disorder can be found in the caption of figure 3(b). The agreement between the predictions of our model and the experimental data is remarkable. In our model, the existence of spin-

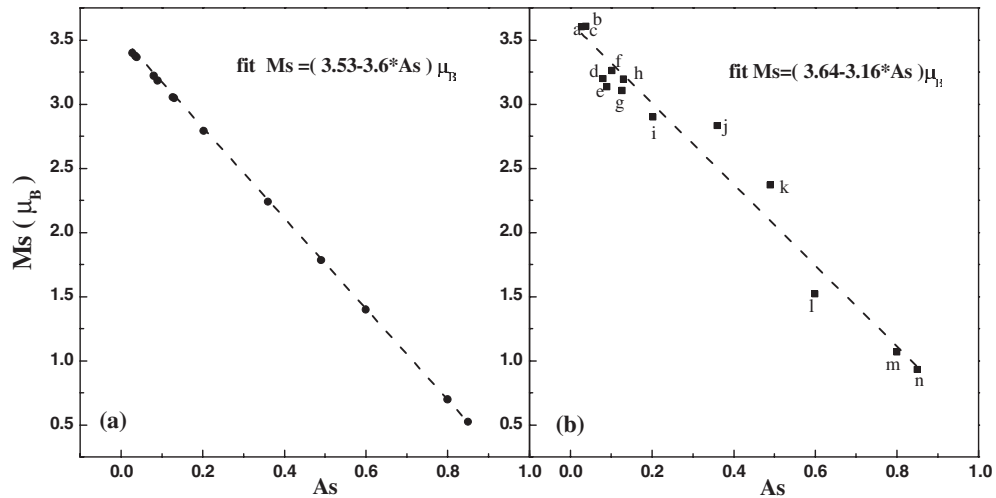


Figure 3. (a) The calculation results of M_s plotted as a function of antisite disorder. (b) Experimental results of low temperature magnetization as a function of the concentration of antisite defects A_s . (a is reproduced from [11]; b, c, f, g are reproduced from [23] d, n, m, l, k, j are reproduced from [24]; i is reproduced from [25].)

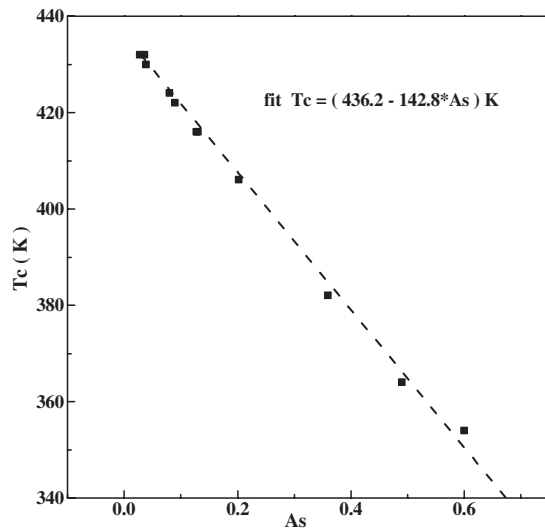


Figure 4. Calculation results of the Curie temperature plotted as a function of antisite disorder.

polarized itinerant carriers is taken into account. Based on this, we have considered the DE interaction mediated by itinerant carriers. The DE ferromagnetic interaction will make parameter b in M_s larger than -8 or -10 in previous theoretical models [5, 9]. In previous theoretical works, only antiferromagnetic interaction was considered. So these results cannot explain the experimental data very well.

The dependence of the Curie temperature on the antisite disorder is shown in figure 4. A linear relation ($T_c = c + d \times A_s$) of the calculated data (dashed line in figure 4) is obtained where parameters $c = 436.2$ and $d = -142.8$. The Curie temperature in Sr₂FeMoO₆ decreases

with the increase of the antisite disorder concentration, which agrees with previous theoretical results [9].

4. Conclusion

In conclusion, we have considered the influence of the itinerant carriers on the saturated magnetization. Moreover, the effect of itinerant carriers on the relation of the magnetization and the antisite disorder is discussed. Both DE interaction and antiferromagnetic coupling between two sublattices are studied by means of the mean field approximation. The temperature dependences of magnetization with and without itinerant polarized carriers have been examined. Because of the existence of the itinerant spin-polarized charge carriers, even in ordered $\text{Sr}_2\text{FeMoO}_6$ the value of M_s cannot reach $4 \mu_B$. Meanwhile M_s depends almost linearly on the antisite concentration A_s ($M_s = a + b \times A_s$, $a = 3.53$, $b = -3.56$). This linear dependence agreed better with the experimental results [11, 23–25] than $M_s = (4 - 10 \times A_s)$ or $(4 - 8 \times A_s) \mu_B$ in previous theoretical models [5, 9].

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