# Green's function method applied to the paramagnetic properties of $R_{1-x}X_xMnO_3$

2009 J. Phys.: Condens. Matter 21 146004

(http://iopscience.iop.org/0953-8984/21/14/146004)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **21** (2009) 146004 (5pp) doi:10.1088/0953-8984/21/14/146004

# Green's function method applied to the paramagnetic properties of $R_{1-x}X_xMnO_3$

**Yuan Chen**[1], **Wen-Fang Xie**[1], **Kang-Xian Guo**[1], **Hong-Dong Liang**[1] **and Ying Xiang**[2]

[1] Department of Physics, Guangzhou University, Guangzhou 510006, People's Republic of China
[2] School of Information Engineering, Guangdong University of Technology, Guangzhou 510006, People's Republic of China

E-mail: newbayren@163.com (Y Chen)

Received 8 October 2008, in final form 18 February 2009
Published 13 March 2009
Online at stacks.iop.org/JPhysCM/21/146004

**Abstract**
The magnetic properties of the isotropic manganites $R_{1-x}X_xMnO_3$ are studied in the paramagnetic regime using the Green's function method. The Curie–Weiss and critical temperatures, $\Theta$ and $T_c$, are obtained within the random phase approximation, as well as the high-temperature susceptibility. Our results are in agreement with other theoretical and experimental results.

## 1. Introduction

Since the discovery of colossal magnetoresistance (CMR) [1, 2] in manganese-based compounds $R_{1-x}X_xMnO_3$ (R = trivalent rare earth, X = divalent alkaline ion), their ferromagnetic to paramagnetic phase transition has been widely studied. Manganites have prompted a burst of research activity in the last decade, as they show not only very rich physics but also possible technological applications. Some of the most prominent conductive and magnetic features of the manganites arise because of the presence of $Mn^{4+}$ ions in addition to $Mn^{3+}$ ions. In the doping range $0.2 < x < 0.5$, these manganites undergo a paramagnetic insulator to ferromagnetic metal phase transition upon cooling, leading to a sharp resistivity peak near the Curie temperature $T_c$ [3].

The dynamics of these systems is mainly governed by the Mn ions, whose average valence changes with $x$ between 4+ and 3+. The $Mn^{4+}$ ions have non-compensated spins in the $t_{2g}^3$ configuration that give rise to localized $S = 3/2$ spins. On the other hand, the $Mn^{3+}$ ions have an extra $e_g$ electron (with $s = 1/2$) that couples ferromagnetically to the $t_{2g}$ spins. The $e_g$ electrons tend to be itinerant and lower their kinetic energy by polarizing with ferromagnetic character the localized $t_{2g}$ spins. This process is known as the double exchange (DE) interaction, which was proposed by Zener [4], and developed by Anderson and Hasegawa [5] and de Gennes [6]. In CMR materials it competes with the classical superexchange interaction between Mn ions [7].

Recently, a quantum form of the Hamiltonian [8] for the DE system, based on the results of the Anderson and Hasegawas semiclassical treatment [5], has been presented. However, in real CMR materials there are a large number of ions and electrons. The hopping of electrons is unavoidably affected by other degrees of freedom, e.g. lattice effect, as pointed out by Millis *et al* [9]. Since the lattice degree of freedom does not need to be added to explain CMR, the Curie temperature $T_c$ obtained from the semiclassical [5] and quantum [8] treatment is much higher than the experimental $T_c$ [9, 10].

It is well known that the ferromagnetic interaction between Mn ions present in CMR perovskites is commonly ascribed to the DE interaction. In order to well describe the magnetic properties of CMR, a simplified model was proposed for this interaction [11, 12]. This model indicates that the hopping of electrons between Mn ions connects them, forming high spin magnetic clusters that include the itinerant electron. The effective ferromagnetic coupling of the Mn ions resulting from this model gives rise to a magnetic susceptibility [12] that may be described by an isotropic Heisenberg-like interaction between $Mn^{3+}$–$Mn^{4+}$ pairs. High-temperature susceptibility in CMR manganites has been studied [7, 13] in the paramagnetic regime by the Weiss mean-field approximation (WMFA) [14], in terms of this kind of effective ferromagnetic Heisenberg-like interaction.

However, since the spin-wave contribution has been omitted, the paramagnetic properties obtained in [13, 7] are the mean-field type results. In this paper, the Green's function method within the random phase approximation (RPA) [15], is used to study the paramagnetic properties affected by the spin wave. The Curie–Weiss and critical temperatures, $\Theta$ and $T_c$, are obtained by the Callen method [16, 17], as well as the zero-field susceptibility $\chi$. Our results for $T_c$ and $\chi$ are in agreement with the other theoretical and experimental results [10, 13].

The paper is organized as follows. In section 2, the formalisms of Green's theory are described, and the basic self-consistent equations are obtained. The analytical results of the susceptibility are presented in section 3. Section 4 contains the discussions and conclusions.

## 2. Model

In this paper we will apply Green's function method to the manganites $R_{1-x}X_xMnO_3$ in the paramagnetic regime. The Hamiltonian for $R_{1-x}X_xMnO_3$ may be described by [11–13] by the three-dimensional mixed-spin Heisenberg model

$$H = -2J\sum_{\langle i,j\rangle}\mathbf{s_i}\cdot\mathbf{S_j} - \mu_B gh\left(\sum_i s_i^z + \sum_j S_j^z\right), \tag{1}$$

where $\mathbf{s_i} = (s_i^x, s_i^y, s_i^z)$ and $\mathbf{S_i} = (S_i^x, S_i^y, S_i^z)$ are the spin $(s, S)$ operators of $Mn^{4+}$ and $Mn^{3+}$ species at site $\mathbf{i}, \mathbf{j}$, with $s = 3/2$ and $S = 2$, respectively. $\langle i, j\rangle$ runs over all possible nearest-neighbor $Mn^{3+}$–$Mn^{4+}$ pairs. $J$ is the nearest-neighbor exchange interaction. The magnetic field $h$ is applied along the $z$ axis. $\mu_B$ and $g$ are the Bohr magneton and the Landé factor, respectively.

In order to calculate the magnetic properties of this model, we introduce the retarded Green's functions as

$$\langle\langle A_i^+(t); e^{aB_j^z}B_j^-\rangle\rangle = -\imath\Theta(t)\langle[A_i^+(t), e^{aB_j^z}B_j^-]\rangle, \tag{2}$$

where $A, B$ denote $s, S$ operators, respectively. $A_i^\pm$ are the spin raising and lowering operators, which are defined by $A_i^\pm = A_i^x \pm \imath A_i^y$ for $A = s, S$, respectively. In equation (2) $\langle Q(t)\rangle$ is defined by

$$\langle Q(t)\rangle = \langle e^{\imath Ht}Qe^{-\imath Ht}\rangle \equiv \frac{\mathrm{Tr}[Q(t)e^{-H/(\kappa_B T)}]}{\mathrm{Tr}[e^{-H/(\kappa_B T)}]},$$

with $\kappa_B$ for the Boltzmann's constant. $\Theta(t)$ is the step function, and $a$ is the Callen parameter [16].

The equations of motion for these Green's functions follow

$$\begin{aligned}\imath\frac{d}{dt}\langle\langle A_i^+(t); e^{aB_j^z}B_j^-\rangle\rangle &= \delta(t)\langle[A_i^+; e^{aB_j^z}B_j^-]\rangle\\ &\quad + \langle\langle[A_i^+(t), H]; e^{aB_j^z}B_j^-\rangle\rangle,\end{aligned} \tag{3}$$

in a straightforward fashion, which are given by, respectively

$$\begin{aligned}\imath\frac{d}{dt}\langle\langle s_i^+(t); e^{as_j^z}s_j^-\rangle\rangle &= \delta(t)\delta_{ij}\theta_s(a) + g\mu_B h\langle\langle s_i^+(t); e^{as_j^z}s_j^-\rangle\rangle\\ &\quad + 2J\sum_\rho[\langle\langle s_i^+(t)S_{i+\rho}^z(t) - s_i^z(t)S_{i+\rho}^+(t); e^{as_j^z}s_j^-\rangle\rangle],\end{aligned} \tag{4}$$

$$\begin{aligned}\imath\frac{d}{dt}\langle\langle S_i^+(t); e^{as_j^z}s_j^-\rangle\rangle &= g\mu_B h\langle\langle S_i^+(t); e^{as_j^z}s_j^-\rangle\rangle\\ &\quad + 2J\sum_\rho[\langle\langle s_{i+\rho}^z(t)S_i^+(t) - s_{i+\rho}^+(t)S_i^z(t); e^{as_j^z}s_j^-\rangle\rangle],\end{aligned} \tag{5}$$

$$\begin{aligned}\imath\frac{d}{dt}\langle\langle S_i^+(t); e^{aS_j^z}S_j^-\rangle\rangle &= \delta(t)\delta_{ij}\theta_S(a)\\ &\quad + g\mu_B h\langle\langle S_i^+(t); e^{aS_j^z}S_j^-\rangle\rangle\\ &\quad + 2J\sum_\rho[\langle\langle s_{i+\rho}^z(t)S_i^+(t) - s_{i+\rho}^+(t)S_i^z(t); e^{aS_j^z}S_j^-\rangle\rangle],\end{aligned} \tag{6}$$

$$\begin{aligned}\imath\frac{d}{dt}\langle\langle s_i^-(t); e^{aS_j^z}S_j^-\rangle\rangle &= g\mu_B h\langle\langle s_i^-(t); e^{aS_j^z}S_j^-\rangle\rangle\\ &\quad + 2J\sum_\rho[\langle\langle s_i^+(t)S_{i+\rho}^z(t) - s_i^z(t)S_{i+\rho}^+(t); e^{aS_j^z}S_j^-\rangle\rangle],\end{aligned} \tag{7}$$

Here $\theta_A(a) = \langle[A^+; e^{aA^z}A^-]\rangle$, and $\theta_A(a = 0) = 2\langle A^z\rangle$ for $A = s, S$, respectively. According to the RPA [15], we approximate the higher-order Green's functions on the right-hand sides of the above equations. The values of $\langle s_i^z\rangle$ and $\langle S_j^z\rangle$ are considered to be independent of their sites, and setting $\langle s_i^z\rangle = m_1$ and $\langle S_i^z\rangle = m_2$ for any site.

After Fourier transforming these equations with respect to the space and time variables,

$$\begin{aligned}\langle\langle A_i^+(t); e^{aB_j^z}B_j^-\rangle\rangle &= \int\frac{d\omega}{2\pi}\int_{1Bz}\frac{d^3\mathbf{k}}{(2\pi)^3}e^{\imath\mathbf{k}\cdot(\mathbf{i}-\mathbf{j})-\imath\omega t}\\ &\quad\times G_{AB}(k,\omega),\end{aligned}$$

we obtain a set of algebraic equations for the transformed Green's functions

$$\omega G_{ss} = \theta_s(a) + g\mu_B hG_{ss} + 2Jm_2\gamma_1 G_{ss} - 2Jm_1\gamma_1(k)G_{Ss}, \tag{8}$$

$$\omega G_{Ss} = g\mu_B hG_{Ss} + 2Jm_1\gamma_2 G_{Ss} - 2Jm_2\gamma_2(k)G_{ss}, \tag{9}$$

$$\omega G_{SS} = \theta_S(a) + g\mu_B hG_{SS} + 2Jm_1\gamma_2 G_{SS} - 2Jm_2\gamma_2(k)G_{sS}, \tag{10}$$

$$\omega G_{sS} = g\mu_B hG_{sS} + 2Jm_2\gamma_1 G_{sS} - 2bJm_1\gamma_1(k)G_{sS}, \tag{11}$$

with

$$\gamma_1(k) = \sum_\rho^{\gamma_1} e^{\imath\mathbf{k}\cdot\boldsymbol{\rho}}, \qquad \gamma_2(k) = \sum_\rho^{\gamma_2} e^{\imath\mathbf{k}\cdot\boldsymbol{\rho}}. \tag{12}$$

Here $\gamma_1 = \gamma_1(k = 0)$ (or $\gamma_2 = \gamma_2(k = 0)$) is the average number of $Mn^{3+}$ (or $Mn^{4+}$) ions surrounding a $Mn^{4+}$ (or $Mn^{3+}$).

The solutions for the transformed Green's functions that are found in equations (8)–(12) can be written as

$$G_{ss}(k,\omega) = \theta_s(a)(\omega - E_s)[(\omega - \omega_k^+)(\omega - \omega_k^-)]^{-1}, \tag{13}$$

$$G_{Ss}(k,\omega) = -2Jm_2\gamma_2(k)[(\omega - \omega_k^+)(\omega - \omega_k^-)]^{-1}, \tag{14}$$

$$G_{SS}(k,\omega) = \theta_S(a)(\omega - E_S)[(\omega - \omega_k^+)(\omega - \omega_k^-)]^{-1}, \tag{15}$$

$$G_{sS}(k,\omega) = -2Jm_1\gamma_1(k)[(\omega - \omega_k^+)(\omega - \omega_k^-)]^{-1}, \tag{16}$$

where

$$\begin{aligned}\omega_k^\pm &= J(m_1\gamma_2 + m_2\gamma_1) + g\mu_B h\\ &\quad \pm J\sqrt{(m_1\gamma_2 - m_2\gamma_1)^2 + 4m_1m_2\gamma_1(k)\gamma_2(k)},\end{aligned} \tag{17}$$

$$E_s = 2Jm_1\gamma_2 + g\mu_B h, \tag{18}$$

$$E_S = 2Jm_2\gamma_1 + g\mu_B h. \tag{19}$$

Using the spectral theorem,

$$\langle \mathrm{e}^{aB_j^z} B_j^- A_i^+(t)\rangle = \imath \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \int_{1Bz} \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \mathrm{e}^{\imath\mathbf{k}\cdot(\mathbf{i}-\mathbf{j})-\imath\omega t} \times \frac{G_{AB}(k,\omega+\imath 0^+) - G_{AB}(k,\omega-\imath 0^+)}{\mathrm{e}^{\beta\omega}-1}, \tag{20}$$

the solutions of the correlation functions $\langle \mathrm{e}^{aA_j^z} A_j^- A_i^+(t)\rangle$ can be obtained, i.e.

$$\langle \mathrm{e}^{aA_j^z} A_j^- A_i^+(t)\rangle = \int_{1Bz} \frac{d^3\mathbf{k}}{(2\pi)^3} \mathrm{e}^{\imath\mathbf{k}\cdot(\mathbf{i}-\mathbf{j})} \frac{\theta_s(a)}{\omega_k^+ - \omega_k^-} \times \left[ \frac{(\omega_k^+ - E_A)\mathrm{e}^{-\imath\omega_k^+ t}}{\mathrm{e}^{\omega_k^+/(\kappa_{\mathrm{B}}T)} - 1} - \frac{(\omega_k^- - E_A)\mathrm{e}^{-\imath\omega_k^- t}}{\mathrm{e}^{\omega_k^-/(\kappa_{\mathrm{B}}T)} - 1} \right]. \tag{21}$$

Here $A = s, S$, respectively.

In order to obtain the sublattice magnetization $m_1 = \langle s_i^z\rangle$ and $m_2 = \langle S_i^z\rangle$, it is convenient to introduce the quantity [16]

$$\Omega_A(a) = \langle \mathrm{e}^{aA^z}\rangle, \qquad A = s, S. \tag{22}$$

Using the self-consistent condition,

$$\langle A_i^- A_i^+\rangle = A(A+1) - \langle A_i^z\rangle - \langle (A_i^z)^2\rangle, \qquad A = s, S,$$

the equal-time auto-correlation functions $\langle \mathrm{e}^{aA_i^z} A_i^- A_i^+\rangle = \theta_A\phi_A$ and $\theta_A = \langle [A^+; \mathrm{e}^{aA^z} A^-]\rangle$ can be written as

$$\theta_A\phi_A = \langle \mathrm{e}^{aA_i^z} A_i^- A_i^+\rangle = A(A+1)\Omega_A - \frac{\partial\Omega_A}{\partial a} - \frac{\partial^2\Omega_A}{\partial a^2}, \tag{23}$$

$$\theta_A = A(A+1)(\mathrm{e}^{-a}-1)\Omega_A + (\mathrm{e}^{-a}+1)\frac{\partial\Omega_A}{\partial a} - (\mathrm{e}^{-a}-1)\frac{\partial^2\Omega_A}{\partial a^2}. \tag{24}$$

Combining equation (21) with equations (22)–(24), we obtain a differential equation for $\Omega(a)$

$$\frac{\partial^2\Omega_A}{\partial a^2} + \frac{(1+\phi_A)\mathrm{e}^a + \phi_A}{(1+\phi_A)\mathrm{e}^a - \phi_A}\frac{\partial\Omega_A}{\partial a} - A(A+1)\Omega_A = 0. \tag{25}$$

Using the Callen method [16], the solution of this differential equation is given by

$$\Omega_A(a) = \frac{\phi_A^{2A+1}\mathrm{e}^{-Aa} - (1+\phi_A)^{2A+1}\mathrm{e}^{(A+1)a}}{[\phi_A^{2A+1} - (1+\phi_A)^{2A+1}][(1+\phi_A)\mathrm{e}^a - \phi_A]}, \tag{26}$$

where $\phi_A$ for $A = s, S$, may be written as

$$\phi_s = \int_{1Bz} \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \frac{1}{\omega_k^+ - \omega_k^-} \left( \frac{\omega_k^+ - E_1}{\mathrm{e}^{\omega_k^+/(\kappa_{\mathrm{B}}T)} - 1} - \frac{\omega_k^- - E_1}{\mathrm{e}^{\omega_k^-/(\kappa_{\mathrm{B}}T)} - 1} \right), \tag{27}$$

$$\phi_S = \int_{1Bz} \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \frac{1}{\omega_k^+ - \omega_k^-} \left( \frac{\omega_k^+ - E_2}{\mathrm{e}^{\omega_k^+/(\kappa_{\mathrm{B}}T)} - 1} - \frac{\omega_k^- - E_2}{\mathrm{e}^{\omega_k^-/(\kappa_{\mathrm{B}}T)} - 1} \right). \tag{28}$$

From equation (26), the sublattice magnetizations $m_1 = \langle s^z\rangle$ and $m_2 = \langle S^z\rangle$ can be found by the differentiation

$$\langle A^z\rangle = \left.\frac{\partial\Omega_A}{\partial a}\right|_{a=0}, \qquad A = s, S.$$

The results are

$$m_1 = \frac{(s-\phi_s)(1+\phi_s)^{2s+1} + (s+1+\phi_s)\phi_s^{2s+1}}{(1+\phi_s)^{2s+1} - \phi_s^{2s+1}}, \tag{29}$$

$$m_2 = \frac{(S-\phi_S)(1+\phi_S)^{2S+1} + (S+1+\phi_S)\phi_S^{2S+1}}{(1+\phi_S)^{2S+1} - \phi_S^{2S+1}}. \tag{30}$$

In order to describe the paramagnetic behavior in the manganese oxides, we consider the system as a randomly distributed mixture of localized $\mathrm{Mn}^{4+}$ and $\mathrm{Mn}^{3+}$ ions [13, 7] with concentrations $x$ and $1-x$, respectively. Thus, the magnetization for one mole $\mathrm{R}_{1-x}\mathrm{X}_x\mathrm{MnO}_3$ sample is given by

$$M = N_{\mathrm{A}}[xm_1 + (1-x)m_2], \tag{31}$$

which may be solved self-consistently by a set of coupled equations (29) and (30). Here $N_{\mathrm{A}}$ is the Avogadro number.

Using equation (31), the susceptibility $\chi = \mathrm{d}M/\mathrm{d}h$ is given by

$$\chi = N_{\mathrm{A}}[x\chi_1 + (1-x)\chi_2], \tag{32}$$

where the sublattice susceptibilities are given by $\chi_1 = \mathrm{d}m_1/\mathrm{d}h$ and $\chi_2 = \mathrm{d}m_2/\mathrm{d}h$, respectively.

## 3. Critical temperature and susceptibility

In this section, we use our solutions of the Green's functions to derive formulae for the critical temperature and susceptibility in the paramagnetic phase.

Fist of all, we estimate the critical temperature $T_{\mathrm{c}}$, which is obtained from the limiting of equations (29) and (30). As the magnetization $M$ approaches zero in the absence of the magnetic field, the equations

$$m_1\phi_s = s(s+1)/3, \qquad m_2\phi_S = S(S+1)/3 \tag{33}$$

are found. These lead to

$$\frac{s(s+1)}{3\kappa_{\mathrm{B}}T_{\mathrm{c}}} = \int_{1Bz} \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \frac{2Jm_1^2\gamma_2}{\omega_k^+\omega_k^-}, \tag{34}$$

$$\frac{S(S+1)}{3\kappa_{\mathrm{B}}T_{\mathrm{c}}} = \int_{1Bz} \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \frac{2Jm_2^2\gamma_1}{\omega_k^+\omega_k^-}. \tag{35}$$

Inserting equation (17) into the above two equations for $h = 0$, we obtain the critical temperature

$$T_{\mathrm{c}} = \frac{2J}{3\kappa_{\mathrm{B}}} \frac{\sqrt{s(s+1)S(S+1)\gamma_1\gamma_2}}{\int_{1Bz} \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \left[1 - \gamma_1(k)\gamma_2(k)/(\gamma_1\gamma_2)\right]^{-1}}. \tag{36}$$

Secondly, above $T_{\mathrm{c}}$, when the applied field $h$ approaches zero, the sublattice susceptibilities become $\chi_1 = m_1/h$ and $\chi_2 = m_2/h$. From equations (17), (29), and (30) we obtain

$$\frac{2s(s+1)J}{3\kappa_{\mathrm{B}}T} = \int_{1Bz} \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \frac{\tilde{\chi}_1(\tilde{\chi}_1\gamma_2 + 1)}{(\tilde{\chi}_1\gamma_2 + 1)(\tilde{\chi}_2\gamma_1 + 1) - \tilde{\chi}_1\tilde{\chi}_2\gamma_1(k)\gamma_2(k)}, \tag{37}$$

$$\frac{2S(S+1)J}{3\kappa_{\mathrm{B}}T} = \int_{1Bz} \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \frac{\tilde{\chi}_2(\tilde{\chi}_2\gamma_1 + 1)}{(\tilde{\chi}_1\gamma_2 + 1)(\tilde{\chi}_2\gamma_1 + 1) - \tilde{\chi}_1\tilde{\chi}_2\gamma_1(k)\gamma_2(k)}. \tag{38}$$

Here $\tilde{\chi}_1 = 2J\chi_1/(g\mu_B)$ and $\tilde{\chi}_2 = 2J\chi_2/(g\mu_B)$. Equations (37) and (38) yield the zero-field relationship

$$\frac{s(s+1)}{S(S+1)} = \frac{\tilde{\chi}_1(\tilde{\chi}_1\gamma_2+1)}{\tilde{\chi}_2(\tilde{\chi}_2\gamma_1+1)}. \tag{39}$$

Combining equations (37) and (38) with (39), after the tedious calculation, the zero-field sublattice susceptibilities $\chi_1$ and $\chi_2$ are given by, respectively

$$\chi_1 = (g\mu_B)^2\frac{s(s+1)}{3\kappa_B T} \times \left[1 + S(S+1)\frac{2J\gamma_1}{3\kappa_B T} + s(s+1)S(S+1)\frac{4J^2F}{9(\kappa_B T)^2}\right], \tag{40}$$

$$\chi_2 = (g\mu_B)^2\frac{S(S+1)}{3\kappa_B T} \times \left[1 + s(s+1)\frac{2J\gamma_2}{3\kappa_B T} + s(s+1)S(S+1)\frac{4J^2F}{9(\kappa_B T)^2}\right] \tag{41}$$

to the second order of $T^{-3}$. Here $F$ is given by

$$F = \gamma_1\gamma_2 - \int_{1Bz}\frac{d^3\mathbf{k}}{(2\pi)^3}\gamma_1(k)\gamma_2(k). \tag{42}$$

Thus, inserting equations (40) and (41) into equation (32), the zero-field susceptibility $\chi$ is calculated to be

$$\chi = \frac{C}{T}\left(1 + \frac{\Theta}{T} + D\frac{\Theta^2}{T^2}\right) \tag{43}$$

to the second order of $T^{-3}$. Here the Curie constant $C$, Curie–Weiss temperature $\Theta$ and coefficient $D$ are given by, respectively,

$$C = N_A(g\mu_B)^2[xs(s+1) + (1-x)S(S+1)](3\kappa_B)^{-1}, \tag{44}$$

$$\Theta = \frac{2J}{3\kappa_B}\frac{s(s+1)S(S+1)[x\gamma_1 + (1-x)\gamma_2]}{xs(s+1) + (1-x)S(S+1)}, \tag{45}$$

$$D = \frac{[xs(s+1) + (1-x)S(S+1)]^2F}{s(s+1)S(S+1)[x\gamma_1 + (1-x)\gamma_2]^2}, \tag{46}$$

and $x$ is the relative concentration of $Mn^{4+}$ ions. This result in equation (43) modifies $\chi = C(T-\Theta)^{-1}$ [13] obtained from WMFA. In the high-temperature region $T \gg \Theta$, the zero-field susceptibility approximately yields WMFA.

## 4. Discussions and conclusions

In this paper we have applied the Green's function method to the manganites $R_{1-x}X_xMnO_3$ in the paramagnetic regime. The Hamiltonian for $R_{1-x}X_xMnO_3$ is described by the three-dimensional mixed-spin Heisenberg model (1). The influence of the spin wave on the magnetic properties is investigated by using RPA. The Curie–Weiss and critical temperatures, $\Theta$ and $T_c$, are obtained.

Assuming a random site occupation [13, 7], the average number of $Mn^{3+}$ (or $Mn^{4+}$) ions surrounding a $Mn^{4+}$ (or $Mn^{3+}$) is $\gamma_1 = (1-x)Z$ (or $\gamma_2 = xZ$). Here $x$ is the relative concentration of $Mn^{4+}$ ions, and $Z$ is the number of nearest Mn neighbors. Then our Curie constant $C$ and Curie–Weiss temperature $\Theta$ agree with the WMFA result [13]. In the very high-temperature limit, our results recover to the Curie–Weiss asymptotic behavior $\chi = C(T-\Theta)^{-1}$.

**Table 1.** Values for the critical temperatures $T_c$. Here $\Theta$ and $T_c^m$ are the measured values of the Curie constant and the critical temperature in [13].

| Compound | $\Theta$ (K) | $T_c^m$ (K) | $T_c$ (K) |
|---|---|---|---|
| $La_{0.67}Ca_{0.33}MnO_3$ | 368 | 260 | 286 |
| $Pr_{0.67}Sr_{0.33}MnO_3$ | 470 | 376 | 366 |
| $La_{0.67}Sr_{0.33}MnO_3$ | 350 | 295 | 272 |

**Table 2.** Values of the susceptibility for $La_{0.67}Ca_{0.33}MnO_3$ at temperatures $T = 450$ and $T = 530$, respectively. The unit for the susceptibility is emu $mol^{-1}$.

| Temperature, $T$ (K) | Our work | WMFA | Ref. [13] | Ref. [8] |
|---|---|---|---|---|
| 450 | 0.015 | 0.032 | 0.023(5) | 0.166 |
| 530 | 0.011 | 0.016 | 0.012(3) | 0.102 |

Using the measured values of the Curie constant $\Theta$ in [13], values of the critical temperature $T_c$ evaluated in equation (36) are shown in table 1. Our $T_c$s are in approximate coincidence with the experimental values [13]. Especially, for $La_{0.67}Ca_{0.33}MnO_3$, our $T_c = 286$ K approximately agrees with the experimental values $T_c = 250$ K [10] and 260 K [13], but disagrees with $T_c = 1050$ K which is calculated from the quantum DE theory [8]. If the quantum DE theory includes the lattice distortion effect [9], band-structure calculations lead to $T_c = 270$ K [8].

In table 2, values of the susceptibility are listed for $La_{0.67}Ca_{0.33}MnO_3$ at temperatures $T = 450$ K and $T = 530$ K, respectively. As compared with the results of WMFA [13, 7, 14] and [8], our results for the susceptibility are closer to the experimental results [13]. In the high-temperature region $T \gg \Theta$, the zero-field susceptibility approximately yields WMFA [13, 7, 14].

It is interesting why the rather simple Hamiltonian (1) is expected to describe the physics of the $R_{1-x}X_xMnO_3$ materials correctly. It is noticed that in CMR materials there are two valences of Mn ions that are responsible for their magnetism [8]. One is $Mn^{4+}$ that has three localized $t_{2g}$ electrons. Another is $Mn^{3+}$ that also has three localized $t_{2g}$ electrons and an itinerant $e_g$ electron. The motion of the $e_g$ electron between two Mn ion neighbors generates the DE interaction. $Mn^{4+}$ is referred to as a d hole with a concentration $x$ in the DE system. Due to the strong Hund coupling ($J_H \to \infty$), in $Mn^{4+}$ the spins of three localized $t_{2g}$ electrons must be parallel and form the core spin $\mathbf{s_i}$ of magnitude 3/2 [9], and in $Mn^{3+}$ the spins of four electrons are also parallel and form the spin $\mathbf{S_j}$ of magnitude 2. In this way, the hopping of an itinerant electron, which is between nearest-neighbor Mn ions, depends on the orientation of the ionic spins $\mathbf{s_i}$ and $\mathbf{S_j}$, according to the DE expression:

$$t_{ij} = t\cos(\theta_{ij}/2),$$

where $\theta_{ij}$ is the relative angle between spins $\mathbf{s_i}$ and $\mathbf{S_j}$, and $t$ is the hopping parameter. Using the relation

$$\cos\theta_{ij} = \mathbf{s_i}\cdot\mathbf{S_j}/(sS),$$

and a standard trigonometric identity for double angles we can write the familiar DE form to be

$$t_{ij} = \frac{t}{\sqrt{2}}\sqrt{1+\frac{\mathbf{s_i}\cdot\mathbf{S_j}}{sS}}. \tag{47}$$

We may then obtain the effective DE Hamiltonian

$$H_{\mathrm{eff}} = \sum_{\langle i,j\rangle}\frac{t}{\sqrt{2}}\sqrt{1+\frac{\mathbf{s_i}\cdot\mathbf{S_j}}{sS}}\,c_i^{\dagger}c_j, \tag{48}$$

where $c_i^{\dagger}(c_j)$ is the operator which creates (destroys) the electron with spin parallel to the localized core spin at the $i$th site. In particular, if the temperature is less than the Fermi temperature of the electrons, $c_i^{\dagger}c_j$ is replaced by the average $\langle c_i^{\dagger}c_j\rangle$ [9]. In the nearest-neighbor Heisenberg model with zero field at $T \geqslant T_c$, $\langle \mathbf{s_i}\cdot\mathbf{S_j}\rangle/(sS) \ll 1$, so an expansion in $\mathbf{s_i}\cdot\mathbf{S_j}/(sS)$ is reasonable. This leads to the effective DE Hamiltonian (48) being reduced to the Hamiltonian (1) if $2J = t\langle c_i^{\dagger}c_j\rangle/(2\sqrt{2})$. However, in [9, 8], the interaction between the core spin of $\mathrm{Mn}^{4+}$ and the $\mathrm{e_g}$ spin of $\mathrm{Mn}^{4+}$ was neglected, and only the contributions of the core spins were considered, which may lead to the great difference between the calculated and measured $T_c$.

In the paramagnetic phase, the DE arising from the hopping of the $\mathrm{e_g}$ electron and its associated lattice distortion [18] is well described by the effective ferromagnetic interaction between $\mathrm{Mn}^{3+}$–$\mathrm{Mn}^{4+}$ pairs (which is $J$ shown in equation (1)). This leads to our results being in agreement with the experimental results [13, 10]. It has been observed that [13] a divergent behavior for the measured susceptibility near $T_c$, in coincidence with the dc magnetic susceptibility, reflects the importance of the ferromagnetic coupling between $\mathrm{Mn}^{3+}$ and $\mathrm{Mn}^{4+}$ ions. It has also been shown in the experiment and theory that [7] the DE interaction may be well represented in terms of the simple two site $\mathrm{Mn}^{3+}$–$\mathrm{Mn}^{4+}$ Heisenberg interaction for doping $x \geqslant 0.15$. Thus, we may conclude that the nearest-neighbor mixed-spin Heisenberg model (1) can describe the physics of $\mathrm{R}_{1-x}\mathrm{X}_x\mathrm{MnO}_3$ materials correctly.

As the microscopic modeling of doped manganites shows [19], CMR manganites are characterized by a complex interplay of charge, spin, orbital, and lattice degrees of freedom. There are several ferromagnetic and antiferromagnetic spin exchange terms—besides the orbital and spin affected hopping. However, in the limit of the strong Hund coupling ($J_{\mathrm{H}} \to \infty$), and averaging over the fermion degrees of freedom, higher-order ferromagnetic and antiferromagnetic spin exchange terms are neglected, and only lower-order ones remain. This leads to the simplified model

$$\begin{aligned} H = {} & -2\sum_{\langle i,j\rangle}\left(J^x s_i^x S_j^x + J^y s_i^y S_j^y + J^z s_i^z S_j^z\right) \\ & - h\left(\sum_i s_i^z + \sum_j S_j^z\right) + 2\sum_{\langle i,i'\rangle} J_{ij}^a \mathbf{s_i}\cdot\mathbf{s_{i'}} \\ & + 2\sum_{\langle j,j'\rangle} J_{jj'}^b \mathbf{S_j}\cdot\mathbf{S_{j'}}. \end{aligned} \tag{49}$$

Here the first term accounts for the ferromagnetic DE interaction. The anisotropic exchange interactions ($J^x$, $J^y$, $J^z$) are responsible for the contributions of the kinetic energy of itinerant electrons, and of the anisotropic hopping between two $\mathrm{e_g}$ orbitals of the nearest-neighbor $\mathrm{Mn}^{3+}$–$\mathrm{Mn}^{4+}$ ions, and of the electron–phonon interaction. The third and fourth terms describe antiferromagnetic superexchange interaction between the local spins of $\mathrm{Mn}^{4+}$–$\mathrm{Mn}^{4+}$ and $\mathrm{Mn}^{3+}$–$\mathrm{Mn}^{3+}$ pairs, respectively. Within the RPA approach, we could give a qualitative estimate of how ferromagnetic DE interaction and antiferromagnetic superexchange interaction will influence $T_c$. The magnetic DE anisotropy (if $J^x \leqslant J^z$, $J^y \leqslant J^z$) tends to suppress the critical fluctuations, and leads to the raising of the critical temperature $T_c$. However, substantial polaronic band narrowing due to strong electron–lattice interaction can prevent ferromagnetic order through $J^z$, and then lead to lower $T_c$. The suppression of ferromagnetic order by antiferromagnetic superexchange interactions may reduce the calculated $T_c$. Thus, if considering anisotropic exchange interactions between $\mathrm{Mn}^{3+}$–$\mathrm{Mn}^{4+}$ pairs, and including the interactions between $\mathrm{Mn}^{3+}$–$\mathrm{Mn}^{3+}$ and $\mathrm{Mn}^{4+}$–$\mathrm{Mn}^{4+}$ pairs in equation (49), our results for $\mathrm{R}_{1-x}\mathrm{X}_x\mathrm{MnO}_3$ will be modified and better agree with the experimental results. These will be discussed in future work.

## Acknowledgments

This work is supported by the National Natural Science Foundation of China under grant Nos 10475021 and 10674033.

## References

[1] von Helmolt R, Wecker J, Holzapfel B, Schultz L and Samwer K 1993 *Phys. Rev. Lett.* **71** 2331

[2] Jin S, Tiefel T H, McCormack M, Fastnacht R R, Ramesh R and Chen L H 1994 *Science* **264** 413

[3] Sheng L, Xing D Y, Sheng D N and Ting C S 1997 *Phys. Rev. Lett.* **79** 1710

[4] Zener C 1951 *Phys. Rev.* **82** 403

[5] Anderson P W and Hasegawa H 1955 *Phys. Rev.* **100** 675

[6] de Gennes P G 1960 *Phys. Rev.* **118** 141

[7] Aliaga H, Causa M T, Tovar M, Butera A, Alascio B, Vega D, Leyva G, Polla G and König P 2003 *J. Phys.: Condens. Matter* **15** 249

[8] Li Q, Ma X and Kou Z 2004 *Phys. Rev.* B **69** 014409

[9] Millis A J, Littlewood P B and Shraiman B I 1995 *Phys. Rev. Lett.* **74** 5144

[10] Lynn J W, Erwin R W, Borchers J A, Huang Q, Santoro A, Peng J-L and Li Z Y 1996 *Phys. Rev. Lett.* **76** 4046

[11] Briático J, Alascio B, Allub R, Butera A, Caneiro A, Causa M T and Tovar M 1996 *Phys. Rev.* B **53** 14020

[12] Allub R and Alascio B 1997 *Phys. Rev.* B **55** 14113

[13] Causa M T, Tovar M, Caneiro A, Prado F, Ibañez G, Ramos C A, Butera A, Alascio B, Obradors X, Piñol S, Rivadulla F, Vazquez-Vazquez C, Lopez-Quintela A, Rivas J, Tokura Y and Oseroff S B 1998 *Phys. Rev.* B **58** 3233

[14] Smart J S 1966 *Effective Field Theories of Magnetism* (Philadelphia, PA: Saunders)

[15] Tyablikov S V 1967 *Methods in Quantum Theory of Magnetism* (New York: Plenum)

[16] Callen H B 1963 *Phys. Rev.* **130** 890
Copeland J A and Callen H B 1966 *Phys. Rev.* **143** 236

[17] Chen Y, Wang Z M and Hu A Y 2005 *Phys. Rev.* B **72** 172406

[18] Huber D L, Alejandro G, Caneiro A, Causa M T, Prado F, Tovar M and Oseroff S B 1999 *Phys. Rev.* B **60** 12155

[19] Weisse A and Fehske H 2004 *New J. Phys.* **6** 158