Magnetic and electronic properties of the new ferrimagnet $Sr_8CaRe_3Cu_4O_{24}$

MASANORI KOHNO[*], XIANGANG WAN, XIAO HU

Computational Materials Science Center,
National Institute for Materials Science, Tsukuba, 305-0047, Japan

Magnetic and electronic properties of the recently-discovered material $Sr_8CaRe_3Cu_4O_{24}$ were investigated by means of a quantum Monte Carlo simulation, the Green function method and the LSDA+U (local spin-density approximation plus the Hubbard-U term) method. The LSDA+U calculation shows that the ground state is an insulator with magnetic moment $M = 1.01$ μ_B/f.u., which is consistent with experimental results. The magnetic sites were specified and an effective model for the magnetic properties of this compound derived. The resultant effective model is a three-dimensional Heisenberg model with spin-alternation. Finite-temperature properties of this effective model are investigated by the quantum Monte Carlo method (continuous-time loop algorithm) and the Green function method. The numerical results are consistent with experimental results, indicating that the model is suitable for this material. Using the analysis of the effective model, some predictions for the material are made.

Key words: *ferrimagnetism; quantum spin system; quantum Monte Carlo*

1. Introduction

Strong electronic correlations produce a rich variety of phenomena. High-T_c superconductivity [1] is one such a phenomenon. It is widely believed that the origin of high-T_c superconductivity is related to the nature of undoped systems [2], which are Mott insulators with an antiferromagnetic order. Recently-discovered perovskite cuprate $Sr_8CaRe_3Cu_4O_{24}$ [3] is a magnetic insulator which has spontaneous magnetization at room temperature and in some respects resembles parent materials of high-T_c superconductors. It is expected that the ferromagnetism of $Sr_8CaRe_3Cu_4O_{24}$ might be caused by strong electronic correlations due to a similar mechanism to the antiferromagnetism of parent materials of high-T_c superconductors. Furthermore, among ferromagnetic cuprates this material has an unusually high magnetic transition tempera-

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[*] Corresponding author, e-mail: KOHNO.Masanori@nims.go.jp

ture (T_c) up to 440 K, although those of other ferromagnetic cuprates are at most 30 K [4]. Thus, the material is interesting for its high T_c induced by strong electronic correlations. The purpose of this paper is to clarify the origin of magnetism and to predict the possible magnetic properties of this material.

2. Local spin-density approximation

The lattice structure is shown in Fig. 1, which is determined experimentally [3]. In order to investigate the electronic properties of the compound, the local spin-density approximation plus the Hubbard-U term (LSDA+U) method using the package WIEN2K [5], which is an implementation of the density-functional APW-lo method
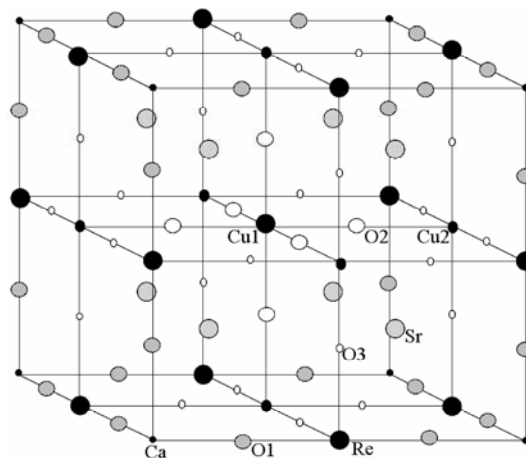

Fig. 1. Unit cell of $Sr_8CaRe_3Cu_4O_{24}$

[6], has been used. The cutoff values were set at $RK_{max} = 7$, the LSDA + U parameters $U = 10$ eV and $J_{LSDA+U} = 1.2$ eV [7]. For the exchange correlation, the standard generalized gradient approximation (GGA) [8] has been applied. The numerical results show that the ground-state is an insulator with a ferrimagnetic order: the charge gap is estimated as about 1.68 eV. Magnetic moments are almost localized at Cu sites, and their directions at Cu1 and Cu2 sites are opposite. The absolute values of the magnetic moments at Cu1 and Cu2 are 1.01 μ_B and 0.86 μ_B per formula unit (f.u.), respectively, and those of other sites are less than 0.07 μ_B/f.u. The total magnetic moment is 1.01 μ_B/f.u., which is comparable to the experimental result (0.95 μ_B/f.u.) [3]. The LSDA+U calculation shows that the orbital degrees of freedom are also ordered. The high T_c could be due to the large overlap between the orbitals of O_2 and Cu originated from orbital ordering. The mechanism of the antiferromagnetic coupling is the super-exchange [9] as in the parent materials of high-T_c superconductors. Details of the LSDA + U calculation are presented in a separate paper [10].

3. Effective model for magnetism

By using LSDA+U method, the magnetic sites of this compound have been identified. Since the system is an insulator, it is natural to expect that the effective model for magnetism is a Heisenberg model. It was assumed that the spins on nearest-neighbour sites interact with each other. Then, the Hamiltonian of the effective model is expressed as

$$H = J \sum_{i,p} \mathbf{S}_i \cdot \mathbf{s}_{i+p/2} \tag{1}$$

where $\mathbf{S}_i$ and $\mathbf{s}_{i+p/2}$ denote spin operators at Cu1 (i) and Cu2 ($i+p/2$) sites, respectively. Here, p represents the unit vectors ($p - \pm\hat{x}, \pm\hat{y}, \pm\hat{z}$). The unit cell of this effective model is illustrated in Fig. 2.
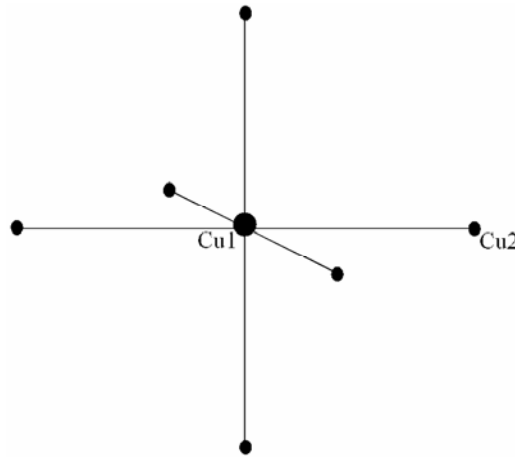

Fig. 2. Unit cell of the effective model

Consider the appropriate combination of spin length (S, s), where S and s denote the spin length at Cu1 and Cu2 sites, respectively. In order to determine these, the magnetization of the ground state (M_{GS}) and that of the fully-polarized state (M_{FP}) for the effective model in a unit cell were calculated. In the case of (S, s) = (1/2, 1/2), $M_{GS} = 1$ and $M_{FP} = 2$, which correspond to 2 μ_B/f.u. and 4 μ_B/f.u., by setting the g-factor 2. For (S, s) = (1/2, 1), (1, 1/2), (1, 1), (M_{GS}, M_{FP}) becomes (5/2, 7/2), (1/2, 5/2), (2, 4), respectively. Here, M_{GS} and M_{FP} obtained by the LSDA+U method are 1.01 μ_B/f.u. and 5 μ_B/f.u.. Hence, (S, s) = (1, 1/2) is the most suitable for this compound.

It should be noted that M_{GS} and M_{FP} of the effective model are exactly 1/2 and 5/2 (equal to 1 μ_B/f.u. and 5 μ_B/f.u.) in any size of system due to the Marshall–Lieb–Mattis theorem [11]. The ground-state magnetization of the effective model (1 μ_B/f.u.) is comparable to the experimental results [3].

Next, the strength of antiferromagnetic coupling J was consdiered. The energy difference between the ground state and the fully-polarized state in a unit cell was calculated by the exact diagonalization method. The result is $8J$. The energy difference was calculated for $Sr_8CaRe_3Cu_4O_{24}$ also by the LSDA+U method. The result was $0.036Ry$. Hence, by comparing these results, $J = 0.0045Ry$ (710 K) was obtained.

4. Green function method

Using the above arguments, the effective model for magnetism of $Sr_8CaRe_3Cu_4O_{24}$, which is a spin-alternating Heisenberg model in three dimensions has been obtained. In order to investigate finite-temperature properties of this compound, the Green function method [12] was applied to the effective model where Green functions are defined as Fourier components of time-dependent correlation functions:

$$G^{Ss}\left(k,\omega\right) = \frac{1}{N}\int dt \sum_{i,j}\left\langle\left\langle S_i^+\left(t\right); s_{j+\frac{p}{2}}^-\right\rangle\right\rangle e^{ik\left(r_i - r_{j+\frac{p}{2}}\right) - i\omega t} \tag{2}$$

Since there are four sites in a unit cell, 16 (4×4) Green functions are necessary. Here, the double-bracket correlation function is defined as

$$\left\langle\left\langle A(t); B\right\rangle\right\rangle \equiv -\theta(t)\left\langle\left[A(t), B\right]\right\rangle$$

Coupled equations were obtained for 16 Green functions by using a decoupling approximation [13]

$$\left\langle\left\langle S^z\left(t\right) s^+\left(t\right); s^-\right\rangle\right\rangle \cong \left\langle S^z\right\rangle\left\langle s^+\left(t\right); s^-\right\rangle$$
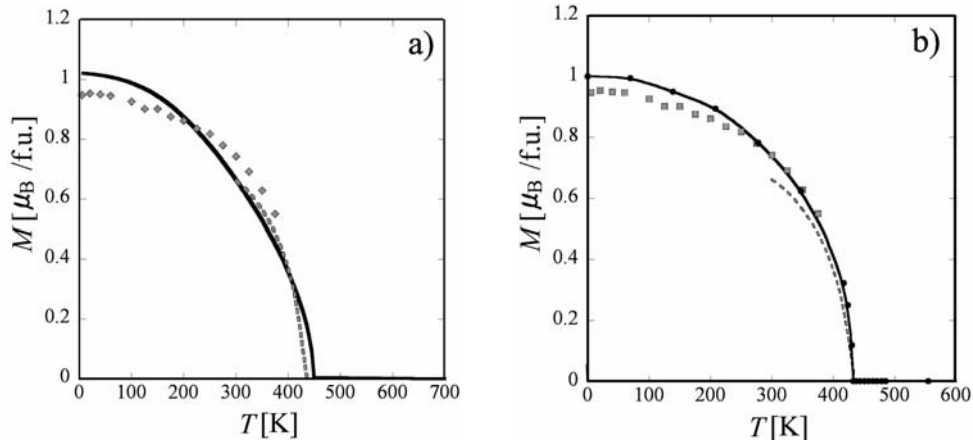

Fig. 3. Temperature dependence of spontaneous magnetization obtained by (a) the Green function method and (b) the quantum Monte Carlo method (solid curves). Dots and dotted line denote the experimental results [3]

These equations were solved analytically and the temperature dependence of magnetizations was obtained using these Green functions by following Callen's scheme [14]. Figure 3a shows the result of the Green function method. The agreement with the experimental result is good, indicating that the effective model is suitable for describing the magnetic properties of $Sr_8CaRe_3Cu_4O_{24}$. From the LSDA+U result J was set as $J = 710$ K.

5. Quantum Monte Carlo simulation

In order to investigate magnetic properties of this compound more quantitatively, a quantum Monte Carlo method was applied to the effective model. The algorithm used was the continuous-time loop algorithm (see Refs. in [15]), which is a powerful method for non-frustrated spin systems. More than one million updates for each simulation were performed. The system size was up to 16×16×16 unit cells which correspond to 16,384 sites.

Spontaneous magnetization can be obtained by extrapolating $\bar{S}(N)$ which is defined as $\bar{S}(N,T) \equiv \sqrt{3\langle S_0^z S_l^z \rangle_T}$, where S_0^z and S_l^z are the z-component of Cu1-spin at the centre of the system and that of the furthest site from the centre, respectively. Here, N denotes the number of unit cells. By extrapolating $\bar{S}(N,T)$ in the thermodynamic limit, we obtain the temperature dependence of spontaneous magnetization as shown in Fig. 3b. The quantum Monte Carlo result is consistent with experimental results. By tuning J to fit the transition temperature, we obtain $J = 695$ K. The first estimation of $J = 710$ K based on LSDA+U results was not far from the fitted value, suggesting that the above mapping is valid. To date, the temperature dependence of the spontaneous magnetization is the only quantity that has been measured experimentally [3]. However, since the effective model for this compound has been derived, further predictions of its magnetic properties through the investigation of this effective model can be made.

The temperature dependence of the inverse of uniform and staggered susceptibilities above the critical temperature are shown in Fig. 4. As is evident from this figure, both susceptibilities diverge toward the critical point. In general, physical quantities show a power-law behaviour at the critical point of the second-order phase transition. The universality class is characterized by the exponents of physical quantities such as length scale $\xi \propto \Delta T^{-\nu}$, magnetization $M \propto |\Delta T|^{\beta}$ and susceptibility $\chi \propto \Delta T^{-\gamma}$, where $\Delta T \equiv T - T_c$. In finite-size systems, the magnetization and the susceptibility can be expressed in terms of scaling functions as [16]

$$M \approx |\Delta T|^{\beta} \bar{M}\left(L|\Delta T|^{\nu}\right) \tag{3}$$

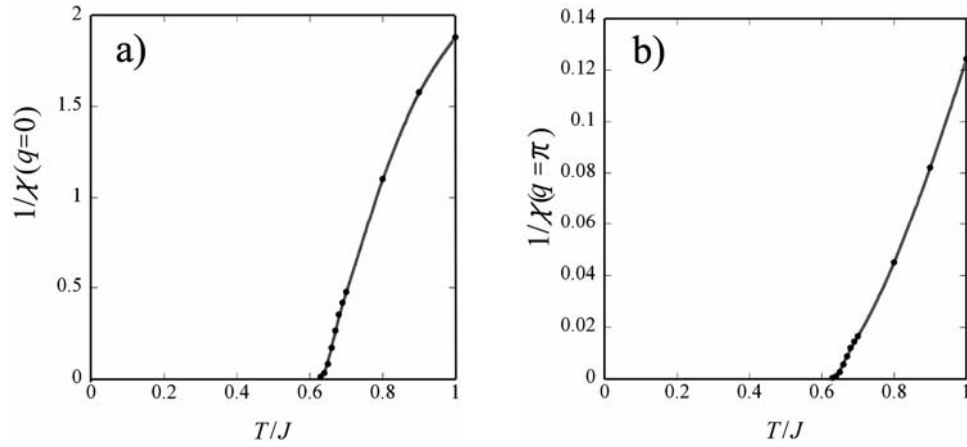$$\chi \approx \Delta T^{-\gamma} \bar{\chi}\left(L\Delta T^{\nu}\right) \tag{4}$$

Fig. 4. Temperature dependence of the inverse of uniform (a)
and staggered susceptibilities (b) above the critical temperature
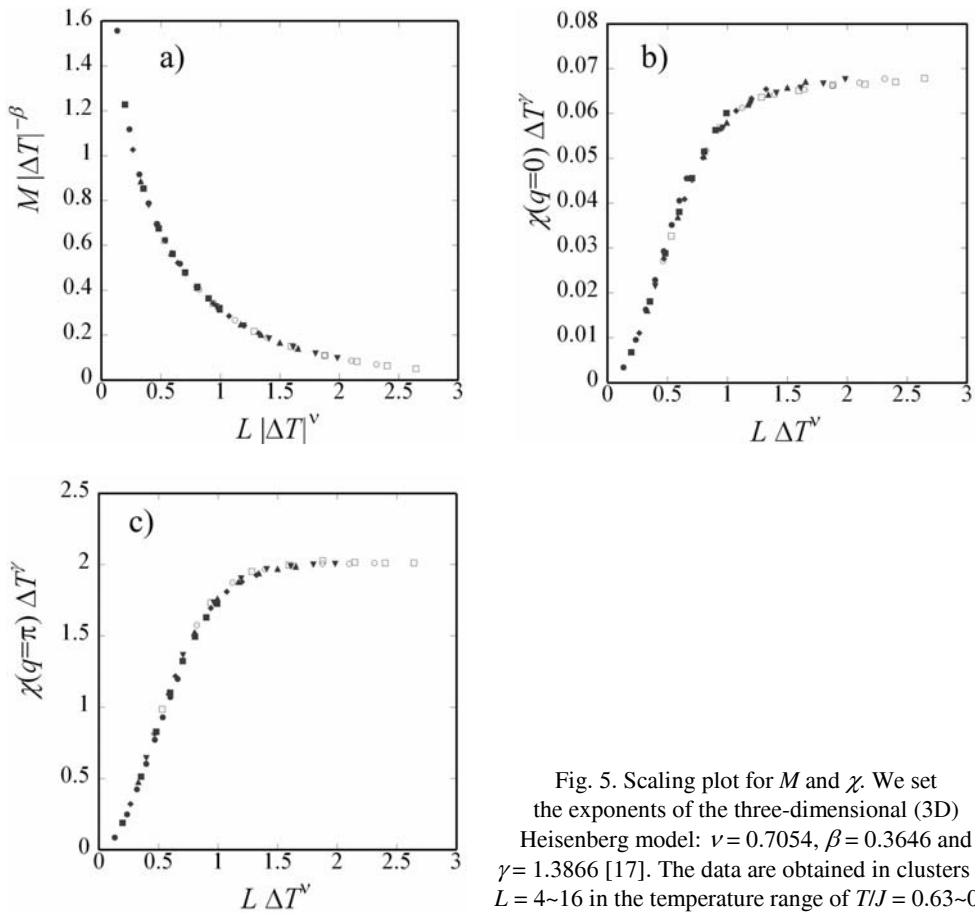

Fig. 5. Scaling plot for M and χ. We set
the exponents of the three-dimensional (3D)
Heisenberg model: $\nu = 0.7054$, $\beta = 0.3646$ and
$\gamma = 1.3866$ [17]. The data are obtained in clusters of
$L = 4\sim16$ in the temperature range of $T/J = 0.63\sim0.7$

$M|\Delta T|^{-\beta}$ and $\chi\Delta T^{\gamma}$ were plotted as a function of $L|\Delta T|^{\nu}$ in Fig. 5, where we use the exponents of the three-dimensional (3D) Heisenberg model: $\nu = 0.7054$, $\beta = 0.3646$ and $\gamma = 1.3866$ [17]. The figure shows that data in various sizes and various temperatures near the critical point fall into single curves, suggesting that the universality class is that of the 3D Heisenberg model.
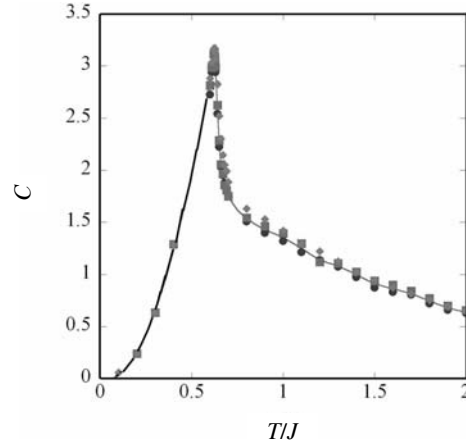

Fig. 6. Temperature dependence of the specific heat. Circles, squares and diamonds denote the data of $L = 12$, 14 and 16, respectively. Solid line is a guide to the eye

The temperature dependence of the specific heat is plotted in Fig. 6. The size dependence of the specific heat is small. The maximum value is almost saturated at about 3.1. The critical temperature was estimated as 0.622 ± 0.002, assuming that the specific heat is a maximum at the critical temperature. Since the specific heat has little size-effect, it is expected that the specific heat at the critical temperature remains finite in the thermodynamic limit. This is consistent with the scaling property of the 3D Heisenberg model: $C \propto \Delta T^{-\alpha}$, $\alpha = -0.1162 < 0$ [17].

6. Conclusions

The magnetic and electronic properties of Sr₈CaRe₃Cu₄O₂₄ have been investigated by means of the quantum Monte Carlo method, the Green function method and the LSDA+U method. Since the LSDA+U calculation shows that magnetic moments are localized at Cu sites, a Heisenberg model was introduced as an effective model for magnetic properties. The spin lengths at Cu1 and Cu2 sites as one and one half, respectively, were obtained by comparing the result given by the effective model in a unit cell and that given by the LSDA+U method. The finite-temperature properties of the effective model were investigated by the Green function method and the quantum Monte Carlo method. The agreement on magnetization at finite temperatures between the numerical results and the experimental results was good, suggesting that the effective model is suitable for describing the magnetic properties of Sr₈CaRe₃Cu₄O₂₄. The

properties of the effective model were further investigated and revealed that the universality class of the critical point is that of the 3D Heisenberg model. Some of the results given by the effective model may be accessible by experiments.

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