The distribution of B-site in the perovskite for a $d^5$-$d^3$ superexchange system studied with Molecular field theory and Monte Carlo simulation

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The B-site disorder in the $d^5$ - $d^3$ system of perovskites has been analyzed with molecular field theory and Monte Carlo method. The model is applicable to $\text{RFe}_{1-p}\text{Cr}_p\text{O}_3$ at any $p$ value. When the saturation magnetization $M_S$ and phase transition temperature $T_P$ are known, a model can be built to calculate the order or disorder distribution of lattice B-sites. We analyze the case that the Fe-Cr superexchange is antiferromagnetic and ferromagnetic coupling respectively. The simulation result shows that the theoretical calculation formula is suitable for the calculation of different B-site distribution. Through the simulation, we find that when the $x$ and $y$ are large, the system will appear obvious long-range order. The DM interaction has a certain influence on the saturation magnetization. Via calculation, we found that the distribution states of Fe and Cr do not always conform to the uniform distribution but rather exhibit an effect that reduces the Fe-Fe clustering. The establishment of this model offers an explanation for several previously contentious issues, e.g., what is the phase transition temperature range of double perovskite, and why the different phase transition temperatures with the same doping proportion. It provides theoretical guidance for the design of functional materials with an arbitrary phase transition temperature.

**Keywords:** B-site disorder distribution, Molecular field theory, Heisenberg Model, Monte Carlo

### I. INTRODUCTION

Perovskite has the formula $\text{RBX}_3$, where R represents nonmagnetic or rare-earth trivalent ions (Bi$^{3+}$, La$^{3+}$, Sm$^{3+}$, Ho$^{3+}$, Gd$^{3+}$, etc.), B denotes trivalent transition metal ions. X is a negative divalent anion, most frequently oxygen ion. The B-site $d^5$-$d^3$ system, commonly Fe$^{3+}$ ($d^5$, $S = 5/2$)-Cr$^{3+}$ ($d^3$, $S = 3/2$), has a cubic-symmetry ideal structure for $\text{RFe}_{1-p}\text{Cr}_p\text{O}_3$. In a ideal structure of $\text{RFe}_9\text{Cr}_9\text{O}_{33}$, Fe$^{3+}$ and Cr$^{3+}$ cations occupy B sites alternately. In this case, the formula can be transformed to $\text{R}_2\text{FeCrO}_6$, a structure known as a double-perovskite. $\text{R}_2\text{FeCrO}_6$, exhibits strong ferromagnetism where the ferromagnetic (FM) coupling exists between Fe$^{3+}$ and Cr$^{3+}$, resulting in a net magnetic moment of 4 $\mu_B$. However, forming the above structure necessitates extremely stringent preparation conditions due to the similar radius of Cr$^{3+}$ and Fe$^{3+}$ ions [1-4]. In reality, the system structure deviates slightly from the ideal structure [5, 6], owing to the disorder of Cr$^{3+}$ and Fe$^{3+}$. It is referred to as anti-site (AS) defects, where Cr$^{3+}$ ions occupy the site previously occupied by Fe$^{3+}$ ions and vice versa. The presence of AS defects significantly reduces the system magnetization. According to the Goodenough-Kanamori (GK) rule [7, 8], Fe$^{3+}$-O-Fe$^{3+}$ and Cr$^{3+}$-O-Cr$^{3+}$ in perovskites are more prone to antiferromagnetic superexchange, and this causes pairwise cancellation of neighboring Fe$^{3+}$/Cr$^{3+}$ moments, significantly reducing the total magnetic moment. In many cases, the saturation magnetic moment of the prepared double perovskite is less than the theoretical magnetic moment; e.g. the theoretical saturation magnetic moment of $\text{Sr}_2\text{FeMoO}_6$ of approximately 4 $\mu_B$, and values greater than 3.8 $\mu_B$ have not been reported [9]. This is interpreted as the AS defects of $\text{Sr}_2\text{FeMoO}_6$. However, this phenomenon is not well understood. This work aims to comprehend what AS defect is, starting from, the fundamental model.

In magnetic analysis, the Heisenberg model is a frequently used model. Exchange interaction theory is based on Heisenberg exchange. The Heisenberg model can be used to demonstrate the effects of AS on magnetic properties more intuitively. In most previous reports, a parameter known as anti-site degree (ASD) is used to describe anti-site defect degree. ASD is defined as the ratio of Cr$^{3+}$ ions occupying the site of Fe$^{3+}$ ions to the total amount of Cr$^{3+}$. We demonstrate in this paper that a single parameter used solely to describe saturation magnetization cannot provide additional information. Indeed, we can approximate the magnetization law of the entire system with only two parameters. The ASD is calculated primarily using the formula $M_S = \mu_{th}(1-2ASD)$ [10], where $M_S$ is the saturation magnetization and $\mu_{th}$

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is the theoretical moment. However, under the antisymmetric anisotropy Dzyaloshinskii-Moriya (DM) interaction \cite{11,12}, antiferromagnetic superexchange possesses a canting moment, conferring the system with weak ferromagnetism (WFM). The DM interaction will affect the ASD calculation in this case. However, the net magnetic moment produced by the DM interaction is often slight, which requires further discussion.

II. MODEL ESTABLISHMENT

A. B-site disorder distribution analysis

The ideal and anti-site structures are depicted in Fig. 1. We mark the blue site in the ideal structure as the \( a \)-site and the green as the \( b \)-site. The \( \text{Fe}^a \) is the name given to \( \text{Fe}^{3+} \) placed in \( a \)-site, and the same is true for \( \text{Fe}^b \), \( \text{Cr}^a \) and \( \text{Cr}^b \). Only \( \text{Fe}^b \) and \( \text{Cr}^a \) have an ideal structure, whereas all \( \text{Fe}^a \), \( \text{Fe}^b \), \( \text{Cr}^a \) and \( \text{Cr}^b \) have an AS defects structure. In this case, the AS defects structure contains four distinct types of nearest superexchange pairs: \( \text{Fe}^a\text{-O-Fe}^b \), \( \text{Fe}^b\text{-O-Cr}^a \), \( \text{Fe}^a\text{-O-Fe}^b \), and \( \text{Cr}^a\text{-O-Cr}^b \). Due to the complexity of the AS defect structure, it is necessary to introduce at least three types of exchange constants, namely \( J_{\text{FC}}, J_{\text{FF}} \) and \( J_{\text{CC}} \), which represent exchange coupling between \( \text{Fe}^{3+} \) and \( \text{Cr}^{3+} \), \( \text{Fe}^{3+} \) and \( \text{Cr}^{3+} \), \( \text{Cr}^{3+} \) and \( \text{Cr}^{3+} \), respectively. In the following, all the \( \text{Fe} \) are abbreviated to \( \text{Fe}^c \), the same as \( \text{Cr} \). The complex magnetic system is based on the interaction of a single site with its adjacent sites. The study of isolated sites is complex and frequently necessitates specialized processing methods. Classical molecular field theory (MFT) is the best solution to approximate the complex magnetic system, typically dividing the crystal into two or more sublattices. This paper studies four sublattices, \( \text{i.e.}, \text{Fe}^a, \text{Fe}^b, \text{Cr}^a, \text{Cr}^b \).

Let \( Z_{ij} \) denote the average number of \( j \)-site surrounding \( i \)-site, \( \text{e.g.}, \) in an ideal structure, \( Z_{\text{Fe}^a\text{Fe}^b} = Z_{\text{Cr}^a\text{Cr}^b} = 6 \). Following the preceding analysis, we can derive the correlating relationship (in AS defects structure) as \( Z_{ij,p} = Z - Z_{ij,p} \), where \( Z \) is the total number of coordination between B-site ions \( Z \) equals six in perovskite. \( i \) and \( j \) represent arbitrary one of \( \text{Fe} \) and \( \text{Cr} \) respectively, and \( i \) and \( j \) are different. Considering the conservation of total exchange pairs, \( \text{i.e.}, \) the number of \( \text{Fe}^a\text{-O-Fe}^b \) pairs is equal to that of \( \text{Fe}^b\text{-O-Fe}^a \), namely

\[ n_i Z_{ij} = n_j Z_{ji}, \]

wherein, \( n_i \) represents the molar fraction of the \( i \)-ion. We define a more general parameter \( f \), which is applicable to any \( p \) in \( \text{FeCr}_1-x\text{Cr}_x\text{O}_3 \) to describe AS defect, as opposed to ASD which is applicable only to double perovskite. The \( f \) factor can be defined as

\[ f = \begin{cases} \frac{n_c}{n_c + n_b} & 0 < p \leq 0.5 \\ \frac{n_f}{n_f + n_b} & 0.5 < p < 1 \end{cases} \]

According to Eq. 2 and the formulas \( n_{\text{Cr}^a} + n_{\text{Cr}^b} = p, n_{\text{Fe}^a} + n_{\text{Fe}^b} = 1 - p \), it can be calculated that

\[ n_{\text{Cr}^a} = pf, \quad n_{\text{Cr}^b} = p(1 - f), \]
\[ n_{\text{Fe}^a} = 0.5 - pf, \quad n_{\text{Fe}^b} = 0.5 - p(1 - f), \]

when \( p \) is less than or equal to 0.5. By combining formula (1), (2), and (3), we can obtain the relation between \( f \) and \( Z_{\text{Fe}^a\text{Fe}^b}, Z_{\text{Fe}^a\text{Fe}^b} \), as well as that between \( Z_{\text{Fe}^a\text{Cr}^b} \) (abbreviated as \( x \)), \( Z_{\text{Fe}^a\text{Cr}^b} \) (abbreviated as \( y \)) and \( Z_{\text{Cr}^a\text{Fe}^b}, Z_{\text{Cr}^a\text{Fe}^b} \).

\[ f = \frac{0.5y - (0.5 - p)x}{p(x + y)} \]

\[ Z_{\text{Cr}^a\text{Fe}^b} = 6 - Z_{\text{Cr}^a\text{Cr}^b} = \frac{2x(1 - p)(6 - y)}{x - y + 2py} \]
\[ Z_{\text{Cr}^a\text{Fe}^b} = 6 - Z_{\text{Cr}^a\text{Cr}^b} = \frac{2y(1 - p)(6 - x)}{y - x + 2px} \]

Until now, all \( Z_{ij} \) and \( f \) factor have been expressed in terms of two parameters, \( x \) and \( y \). Additionally, as the value of \( Z_{ij} \) is limited between 0 and 6, and the value of \( f \) is limited between 0 and 1, the range of values for \( x \) and \( y \) are determined, that is,

\[ \begin{cases} x(1 - p)(6 - y) \leq 3(x - y + 2py) \\ y(1 - p)(6 - x) \leq 3(y - x + 2px) \end{cases} \]
\[ 0 \leq x \leq 6 \]
\[ 0 \leq y \leq 6 \]

within the above constraints, \( x \) and \( y \) can be adjusted arbitrarily.

The ideal double perovskite structure is shown in Fig. 2 (a), where \( y \) can be any value. When \( x \to 6 \) and \( y \to 6 \), the Fe-rich and Cr-rich phenomena are evident. One could even call that the system contains two independent phases with \( \text{Fe}^{3+} \) and \( \text{Cr}^{3+} \) occupying one side, as illustrated in Fig. 2(b). \( x \to 0, y \to 6 \) is depicted as in Fig. 2(c), the anti-site atoms essentially do not exist, \( \text{i.e.}, \) it can be ignored \( \text{Fe}^{3+}\text{-O-Fe}^{3+} \) or \( \text{Cr}^{3+}\text{-O-Cr}^{3+} \) exchange. When \( x \to 3 \) and \( y \to 3 \), the arrangement tends to disorder (Fig. 2(d)), this situation corresponds to the case of uniform distribution. The preceding rules can be summarized in the following manner. When \( x \) and \( y \) are both...
Step 5. repeat Step 4 until $\rho$ is 0. Go through the above five steps to obtain the lattice distribution of the specified coordination.

In order to investigate the effect of disorder on the magnetic properties of perovskite, we will consider DM interaction. The Hamiltonian of the system can be expressed as

$$\mathcal{H} = -\sum_{\langle i,j \rangle} J_{ij} S_i S_j - \sum_{\langle i,j \rangle} D_{ij} (S^z_i S^z_j - S^z_i S^z_j)$$

wherein, $S_i$ is the pseudospin vector and let $S_F = 5/2$, $S_C = 3/2$. $\langle i,j \rangle$ represents the nearest neighbour of $i$ is $j$ ion, the $J_{ij}$ is the exchange constant between $i$ and $j$ ions. $D_{ij}$ is the DM interaction vector. There is a cross product in the above Hamiltonian. In order to simplify the calculation, we only study the DM interaction in the $z$-axis. So, the Hamiltonian can be rewritten as

$$\mathcal{H} = -\sum_{\langle i,j \rangle} J_{ij} S_i S_j - \sum_{\langle i,j \rangle} \left| F_{ij} \right| \left( S^z_i S^z_j - S^z_i S^z_j \right)$$

The $D_{ij}$ in formula (6) is an antisymmetric parameter, i.e., $D_{ij} = -D_{ji}$. In this work, we let $|D_{FC}| = |D_{CC}| = |D_{FF}| = D$ to reduce the number of parameters.

C. Analyze the relationship between $T_P$, $M_S$ and parameters $x$, $y$

We establish four sublattices to calculate the phase transition temperature, ignoring the effect of DM interaction to reduce computational complexity. Each sublattice has an energy value:

$$H_{F^a} = \lambda_{F^a} M_{F^a} + \lambda_{F^a} C^a M_{C^a} + H$$
$$H_{F^b} = \lambda_{F^b} M_{F^b} + \lambda_{F^b} C^b M_{C^b} + H$$
$$H_{C^a} = \lambda_{C^a} M_{C^a} + \lambda_{C^a} M_{C^b} + H$$
$$H_{C^b} = \lambda_{C^b} M_{C^b} + \lambda_{C^b} M_{C^a} + H$$

where $\lambda_{ij} = 2Z_{ij} J_{ij}/n_i N_A (g\mu_B)^2$ is the molecular field coefficient of $j$-sublattice relative to $i$-sublattice. Here $J_{ij}$ denotes the exchange constant between $i$- and $j$-ions, $g$ is the Lande factor, $\mu_B$ represent Bohr magneton. $H$ is the external magnetic field. $M_i$ represents the magnetization of $i$-sublattice. The magnetization of $i$-sublattice $M_i$ is

$$M_i = n_i N_A g\mu_B S_i B_{ij} \left( \frac{g\mu_B S_i H_i}{k_B T} \right)$$

where $B_{ij}(\gamma)$ is the Brillouin function. Near the phase transition temperature $\gamma \ll 1$. The Brillouin function can be reduced to the first term of Taylor expansion as $B_{ij}(\gamma) \approx \gamma(J+1)/3J$. Let $H = 0$, simultaneous equation (6) (7) and (8), solve the relation of $M_i$ and include the coefficient of $M_i$ in the determinant $A$. Let the determinant $A$ be 0, i.e.,
The solution $T_P$ of equation (9) is

$$T_P = \frac{1}{2k_B} \sqrt{A_{12}A_{21} + A_{14}A_{41} + A_{23}A_{32} + A_{34}A_{43}}$$

$$+ \frac{(A_{12}A_{21} + A_{14}A_{41} + A_{23}A_{32} + A_{34}A_{43})^2}{4(A_{14}A_{23} - A_{12}A_{34} - A_{14}A_{23})}$$

where $A_{ij}$ is the item of row $i$ and column $j$ of the determinant $A$. To calculate the saturation magnetization in the ground state with DM interaction, the direction of the magnetic moment of each sublattice needs to be considered first. The canted angle is defined with the smallest energy. All spins on each sublattice should point in the same direction in the ground state. In the $xoy$ plane, the energy $E$ per site for the system is

$$E = \frac{1}{N} \left( k_1 (J_{FF} \cos \alpha_{FF} + D_{FF} \sin \alpha_{FF}) + (k_2 + k_3) J_{FC} \cos \alpha_{FC} + (k_2 + k_3) D_{FC} \sin \alpha_{FC} + k_4 (J_{CC} \cos \alpha_{CC} + D_{CC} \sin \alpha_{CC}) \right)$$

where

$$k_1 = Z_{p,s,p_s,p_s} S_{Fe}^2, \quad k_2 = Z_{c,p,c_s,p_s} S_{Cr} S_{Fe}, \quad k_3 = Z_{c,p,c_s,c_s} S_{Cr} S_{Fe}, \quad k_4 = Z_{c,c,c,c} S_{Cr} S_{Fe}$$

$\alpha_{FF}$, $\alpha_{FC}$, $\alpha_{CC}$ satisfy relation $\alpha_{FC} = \frac{\alpha_{FF} + \alpha_{CC}}{2}$, see in Fig. 3. In order to solve the canted angles, three canted angles that minimize the Hamiltonian must be found [13], namely, let

$$\frac{\partial E}{\partial \alpha_{FF}} |_{\alpha_{FF}=\alpha_1} = 0, \quad \frac{\partial E}{\partial \alpha_{CC}} |_{\alpha_{CC}=\alpha_3} = 0$$

It is well established that the canted angle caused by DM interaction is extremely small. We use the Taylor approximation to solve the above $\alpha_{FF}$, $\alpha_{FC}$, $\alpha_{CC}$, putting $\theta_{ij} = \pi - \theta_{ij}$ into Eq. 11, and taking $\cos \theta_{ij} \approx 1 - \frac{\theta_{ij}^2}{2}$, $\sin \theta_{ij} \approx \theta_{ij}$. To solve a solution of

$$\alpha_{FF} = \frac{D_{FF} J_{FC} k_1 (k_2 + k_3) + D_{CC} J_{FC} k_4 (k_2 + k_3)}{J_{CC} J_{FC} k_4 (k_2 + k_3) + 4 J_{CC} J_{FF} k_1 k_4 + J_{FC} J_{FF} k_1 (k_2 + k_3) + \pi}$$

$$+ \frac{J_{CC} J_{FC} k_4 (k_2 + k_3) + 4 J_{CC} J_{FF} k_1 k_4 + J_{FC} J_{FF} k_1 (k_2 + k_3)}{2 J_{FC} J_{FF} k_1 (k_2 + k_3) + 4 J_{CC} J_{FF} k_1 k_4 + \pi}$$

$$\alpha_{CC} = \frac{J_{CC} J_{FC} k_4 (k_2 + k_3) + 4 J_{CC} J_{FF} k_1 k_4 + J_{FC} J_{FF} k_1 (k_2 + k_3)}{2 J_{FC} J_{FF} k_1 (k_2 + k_3) + 4 J_{CC} J_{FF} k_1 k_4 + \pi}$$

FIG. 3. Schematic diagram of competition between two sublattices with different canted angles for DM interaction on the same site.

The net magnetic moment can be calculated by the superposition of plane coordinate vectors, as illustrated in Fig. 3. Let $M_{Fe} = (n_{p,Fe} S_{Fe}, 0)$, $M_{Fe'} = (n_{p,Fe'} S_{Fe'} \cos \alpha_{FF}, n_{p,Fe'} S_{Fe'} \sin \alpha_{FF})$, $M_{Cr} = (n_{c,Cr} S_{Cr} \cos \alpha_{FF}, n_{c,Cr} S_{Cr} \sin \alpha_{FF})$, $M_{Cr'} = (n_{c,Fe'} S_{Fe'} \cos (\alpha_{FF} - \alpha_{FC}), n_{c,Fe'} S_{Fe'} \sin (\alpha_{FF} - \alpha_{FC}))$. The net moment is

$$M_{net} = \sqrt{A_1 + A_2}$$

where

$$A_1 = [n_{p,Fe} S_{Fe} + n_{p,Fe'} S_{Fe'} \cos \alpha_{FF} + n_{c,Fe} S_{Cr} \cos \alpha_{FC} + n_{c,Fe} S_{Cr} \sin \alpha_{FF} - n_{c,Fe} S_{Cr} \sin (\alpha_{FF} - \alpha_{FC})]^2$$

The above calculation is only applicable to the analysis of Fe-O-Cr antiferromagnetic superexchange. To verify the accuracy of the above theory, we use Monte Carlo method to simulate different coordination $x$, $y$ and proportions $p$.

D. Monte Carlo simulation

We simulate the Heisenberg model using Monte Carlo method based on the Metropolis Hastings criterion. To minimize the time overhead, we optimize the calculation using the parallel chessboard algorithm [14] and Gaussian adaptive sampling [15]. Set $L$ equal to 20, as there is no discernible difference between $L$ values greater than 20 [16]. According to the Metropolis Hastings criterion, the flip probability $P$ is

$$P = e^{-\frac{\Delta H}{k_B T}}$$

where $k_B$ is Boltzmann constant and $\Delta H$ is the energy difference between the per- and post-flip states. $M$
should be calculated as

$$M = \sqrt{m_x^2 + m_y^2 + m_z^2} \quad (14)$$

wherein

$$m_\alpha = \frac{1}{L^3} \sum_{i=1}^{L^3} S_i^\alpha, (\alpha = x, y, z)$$

The susceptibility $\chi$ of this system is a key parameter, which reflects the phase transition, that is described as

$$\chi = \frac{\partial M}{\partial H} = \frac{L^3 (\Delta M)^2}{k_B T} = \frac{L^3 \langle M^2 \rangle - \langle M \rangle^2}{k_B T} \quad (15)$$

where $i$ represents the $i$-th thermodynamic statistical time. The entire simulation process requires performing flip judgments in a loop; when the loop runs for $L^3$ time, the entire process is referred to as one Monte Carlo step (MCs). We use $10^4$ MCs to bring the system to equilibrium, and $10^5$ MCs to calculate statistics.

III. RESULT AND DISCUSSION

Figure 4 illustrates the situation of two orbit coupling, in which, $p\sigma$ orbit coupling is the leading factor in Fe-O-Cr FM superexchange. When the bond angle $\theta$ is between $142^\circ < \theta < 156^\circ$ [17, 18], the orbital coupling transforms as $p\sigma$, and the Fe-O-Cr coupling transforms to AF superexchange. The sign of the Fe-O-Cr superexchange coupling constant has been controversial. This superexchange coupling constant is different in many materials. We will avoid debating this point, and instead, study AS in two situations. The $J_{CC}$ is negative sign according to the Goodenough-Kanamori (GK) [7,8], the same holds true for $J_{FF}$. To be consistent with reality, we set $J_{FF} = 1.5J_{CC}$ and $|J_{FC}| = 0.5|J_{CC}|$ to maintain the isometric relationship between the three exchange constants.

For the magnetization curve under various coordination relations, see Fig. 5. When $f$ equals 0.4, the saturation magnetization is approximately 0.1, which is attributed to the AF superexchange coupling between Fe and Cr. In any case, all ions in $a$-site always point in the same direction, the same is true of $b$-site. When $f$ is equal to 0.4, 40% of Cr occupies the $b$-site and 60% Cr occupies the $a$-site. The total moment is easily calculated to be 0.625 in the $a$-site, and 0.525 in the $b$-site. The difference between the moments of $a$- and $b$-site is the net moment. Therefore, the saturation magnetization $M_S$ in $\text{RFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ can be summarized as follows:

$$M_S = \left| \frac{1 - 2f}{2} \right| \quad (16)$$

The inset of Figure 5 (a) shows the general rule, which states that the greater the $y$, the higher the phase transformation temperature.

![FIG. 4. Schematic diagram of the two kinds of orbit coupling](image)

**FIG. 4.** Schematic diagram of the two kinds of orbit coupling

![FIG. 5. Temperature dependence of magnetization under the same ASD and different coordination number. (a) in the case of the AF superexchange coupling between Fe and Cr, i.e., $J_{FC} < 0$. (b) in the case of the FM superexchange coupling between Fe and Cr, i.e., $J_{FC} > 0$. Insets are the susceptibility with different $y$, which correlating to the M-T.](image)

**FIG. 5.** Temperature dependence of magnetization under FM superexchange coupling between Fe and Cr. The saturation magnetization is approximately 0.4, which is in the presence of exchange competition. However, there is a dominant tendency in this competitive relationship when the degree of dislocation is small. If $f = 0$, the magnetic moments of the a-
and b-site point in the same direction. When \( f = 0.4 \), 40\% Fe\(^b\) takes the place of Cr\(^a\). After replacement, the magnetic moment is oriented in the opposite direction to the original magnetic moment orientation. Because the competitive trend dominated by antiferromagnetic interaction maintains the opposite magnetic moment orientation, as shown in Fig. 6. From this, it is calculated that the moment on \( a\)- and \( b\)-site is roughly

\[
\begin{align*}
a\ -\ site: \quad M^a &= \frac{3}{4} (1 - f) - \frac{5}{4} f = \frac{3}{4} - 2f \\
b\ -\ site: \quad M^b &= \frac{5}{4} (1 - f) - \frac{3}{4} f = \frac{5}{4} - 2f
\end{align*}
\]

The saturation magnetization \( M_S \) is sum of \( M_a \) and \( M_b \), i.e.,

\[
M_S = 2 - 4f \tag{17}
\]

Formula (16),(17) consistent with the formula in Ref. 10 and the formula (12) when \( D = 0 \).

FM superexchange coupling uses a phase transformation mechanism similar to that of AF superexchange coupling between Fe and Cr. It is worth noting that when \( y \) is less than or equal to 4, the magnetic susceptibility peak value exhibits some deviation. While this appears to contradict molecular field theory, it is merely an illusion of frustrated magnetic susceptibility. In the frustrated state, the magnetic susceptibility peak temperature may deviate from the phase transition temperature, which must be determined precisely using heat capacity or fourth-order Binder cumulants.

![Lattice distribution with magnetic moment orientation in the presence of AS defects.](image)

**FIG. 6.** Lattice distribution with magnetic moment orientation in the presence of AS defects.

The relationship between magnetization and temperature for various \( f \), as shown in Fig. 7(a). All saturation magnetizations in the AF superexchange coupling, are in accordance with the formula (4). Let \( J_{CF} = 1.5J_{CC} \), \( J_{FC} = 0.5J_{CC} \), \( p = 0.5 \), and \( y = 3 \), we can calculate

\[
T_P = \frac{5 \sqrt{3} \sqrt{393x + \sqrt{(15x^2 + 99x + 567)} \ (7x^2 + 687x + 63) + 7x^2 + 315}}{48k_B} \tag{18}
\]

![The plot of the dependence of magnetization on temperature under different \( f \) values.](image)

**FIG. 7.** The plot of the dependence of magnetization on temperature under different \( f \) values. The \( x \) is equal to from 1 to 6 marked in the figure correspond to \( f = 0.25, 0.40, 0.50, 0.57, 0.63 \) and \( 0.67 \), respectively. (a) the plot in the case of \( J_{CF} < 0 \). (b) the plot in the case of \( J_{CF} > 0 \).

There are discrepancies in phase transition temperature calculated between Heisenberg model and MFT under the same parameters. Thus the phase transition temperature calculated by MFT requires a series of transformations to apply to the Heisenberg model simulated by Monte Carlo method. The phase transition temperature calculated using MFT is well known to be proportional to the exchange constant. The same is true for the Heisenberg model [19]. Consequently, the phase transition temperature determined by MFT is proportional to that determined by Heisenberg model. Due to the ignorance of thermal disturbance by MFT, the phase tran-
transition temperature calculated by MFT is much higher than that of the Heisenberg model. We set a scale factor $\xi$ for conversion, i.e., $T_P^H = \xi T_P$. $\xi$ is independent of temperature but depends on the parameters of critical size $L$, proportion $p$ and spin value $S$. We set $\xi(L) = \varepsilon(L) \frac{S_F(S_F+1)(1-p)+S_C(S_C+1)p}{2}$, the accuracy of the model is validated by fitting method. Through fitting the simulation data under the conditions that $y = 3$, $J_{FF} = -1.5$, $J_{CC} = -1$, $J_{FC} = -0.5$, and $p = 0.5$, the calculated the value of $\xi$ is 0.202 and $\varepsilon$ is 0.032, at $L = 20$, as see in Fig. 8.

Figure 7(b) shows the M-T curve under FM superexchange coupling in Fe-O-Cr. We discovered an intriguing phenomenon in Fig. 7(a) and (b), i.e., when $x = 3$, the magnetization is close to zeros. We can deduce from equal (12) that the $M_S$ under $x = 3$ is zeros. Indeed, both magnetization and susceptibility exhibit antiferromagnetic properties. Notably, $x = 3$ and $y = 3$ are the most frequently occurring coordination numbers in a completely random system. According to numerous reports, when Cr/Mn is doped with Fe perovskite, the coordination relationship between Cr/Mn and Fe follows a binomial distribution [4]. In this case, the mean value of the coordination number all be three, i.e., $x = y = 3$. However, no experiment has observed that the magnetization tends to zero. This subject will be discussed in greater detail below. Notably, when $x$ is greater than 4, the magnetization exhibits the long-range order phenomenon near the phase transition temperature. Magnetic susceptibility peaks become extremely broad. This could be caused by the presence of a high degree of clustering. When $x$ approaches six, partial Fe-Fe clusters dubbed Fe-rich, form. The phase transition temperature increases as the Fe-O-Fe interaction increases. Weak Fe-O-Cr interaction reduces the phase transition temperature in part of the Fe-O-Cr interaction. They are in competition with one another, leading to long-range order.

As previously stated, the magnetization is close to zero when $x = y = 3$. However, because of the DM interaction, the canting moment induces weak ferromagnetism (WFM) in the entire system, as illustrated in Fig. 9. This appears to account for the absence of experimental evidence for extremely weak saturation magnetization. Fe-O-Cr Antiferromagnetic coupling occurs between adjacent sites as a result of the Fe-O-Cr AF superexchange interaction. The net moment is increased as a result of the DM interaction. The inset of Figure 9(a) shows the susceptibility at various D values; the value of D has little effect on the magnetic susceptibility peak position, indicating that the size of D has little effect on the phase transition temperature.
Indeed, when Fe-O-Cr is FM superexchange, the sublattice moments of F⁰ and C⁰ are in the same direction but are in opposition to those of F³ and C³. Marking that the sublattice of F⁰ and C⁰ is B₁, and C³ and F³ are B₂. When B₁-O-B₂ exists, the DM interaction generates a net moment in the same direction. When there is B₁-O-B₁ or B₂-O-B₂, however, the DM interaction reduces the magnetic moment, and points in the direction perpendicular to the net moment of B₁-O-B₂ as shown in Fig. 10. Furthermore, the net magnetic moment produced by this DM interaction is quite small, with a normal D value of approximately 0.01 (in the order of magnitude in this paper). Thus, the effect of DM interaction, in this case, could be ignored. Moreover, there are two phase transition temperatures exhibited in the inset of Figure 9(b). The two humps may correspond to Neel temperature $T_N$ and Curie temperature $T_C$, respectively.

The expected nearest number $E_k$ of Cr³⁺ ions around one Fe³⁺ ion is

$$E_k = \sum_{k=1}^{6} k P(k) = 3$$

$$E_k = \frac{6-x}{n_{F^3}} + \frac{6-y}{n_{F^3}}$$

When the system is uniformly distributed, due to the symmetry of the sites, $n_{F^3} = n_{F^3}$ and $x = y$. According to Eq. 12, $x = y = 3$ can be determined. We can calculate that the phase transition temperature in $J_{FF}/k_B = -21.14$ K, $J_{CC}/k_B = -17.06$ K under uniform distribution ($x = y = 3$), is $\sqrt{525 J_{FC}(1+\Delta)^2} + 248.95$ K, indicating that the phase transition temperature is at least 370 K. From this point, the discrepancy of ion radius between Cr and Fe, the disorder in the majority reaction process does not conform to the uniform distribution. LaFe₀.₅Cr₀.₅O₃ in the study of Paul Blessington Selvadurai A et al. [28] is proved to be disordered; the phase transition temperature is about 380 K according to our observation. We can reasonably assume that Fe and Cr are distributed.

![Diagram](image)

**FIG. 10.** Discrepancy magnetic moment directions produced by DM interaction between AF and FM.
uniformly in this system; $J_{FC}/k_B$ is calculated to be about 4.4 K, which corresponds to the $T_P$ of La$_2$FeCrO$_6$ of about 101 K and is very close to the conclusion of Pio Baetting. According to the formula (10), different $x$ and $y$ values will correspond to different phase transformation temperature. We plot the phase transition temperature in Fig. 11 and observe that the phase transition temperatures are basically concentrated in the middle of the whole curved surface. In most cases, it should follow some statistical distribution, whereas it does not follow a perfect uniform distribution. The formula (110) is quite complex, but Fig. 11 shows a monotonous trend as a whole. Two extreme values are taken at $x = 0, y = 0$ and $x = 6, y = 6$, respectively. We calculate the two cases and the results are $5\sqrt{21}J_{FC}$ and max $(35J_{FF}, 15J_{CC})$. This indicates that in a disordered system, $J_{FC}$ is less than $T_P/5\sqrt{21}$, which is used to distinguish the exchange constant of double perovskite.

![FIG. 11. The plot of phase transition temperature $T_P$ surface corresponding to different $x$ and $y$ at $p = 0.5$.](image)

**IV. CONCLUSION**

In conclusion, we have used the MFT algorithm and established a four-sublattice model suitable for the disordered system. By deducing the phase transition temperature and net magnetic moment equations, the coordination of a chaotic system can be calculated if $T_P$ and $M_S$ are known. We have tested it using the Monte Carlo method; the results are excellent and consistent with our expectations. We use Monte Carlo method to simulate the effect of different B-site distribution and DM interaction on magnetic properties. The magnetic properties are sensitive to the values of $x$ and $y$. Larger $x$ and $y$ will trigger the long-range order of B-site magnetic ions. Additionally, our analysis reveals that the distribution of Fe / Cr in the majority of systems deviates from the uniform distribution, namely $x = y = 3$. In addition, we predict that the phase transition temperature of the ideal La$_2$FeCrO$_6$ double perovskite system is about 101 K based on this model. This model offers quantitative calculation method for B-site disorder system. It provides a new method for the quantitative calculation of magnetoelectric coupling in B-site disordered system.

**V. DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**VI. COMPETING INTERESTS**

The Authors declare no Competing Financial or Non-Financial Interests.

**VII. AUTHOR CONTRIBUTIONS**

The first author, Jiajun Mo, is responsible for programming, modeling, analysis and writing. Co-first author Min Liu is responsible for modeling and analysis, as well as result calculation, he has the same contribution as the first author. The third author, Shiyu Xu, is responsible for searching the literature, drawing and adjusting and revising the papers. The forth, fifth, sixth authors, Qinghang Zhang, Jiyu Shen and Puyue Xia put forward the improvement scheme for the paper respectively. First correspondent, Yanfang Xia, is the main director of this project. The second correspondent, Jizhou Jiang, provided technical support for the project.

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