Spin glass state and enhanced spiral phase in doped delafossite oxide CuCrO$_2$

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In this paper, we study the doping effects on the magnetic states of CuCrO$_2$ based on the classical frustrated spin model [Lin et al., Phys. Rev. B 89, 220405(R) (2014)]. Several experimental observations can be well reproduced by the Monte Carlo simulations of the modified spin models. Our paper suggests that the disorder induced by V/Al doping cooperating with the frustration in the system may contribute to the emergence of the spin glass state. Furthermore, the hole doping by Mg$^{2+}$ substituting Cr$^{3+}$ enhances the quantum fluctuations and bond disorder which modulate the biquadratic exchanges and in turn results in the promotion of the spiral phase, consistent with the experimental report.

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I. INTRODUCTION

During the past decades, nontrivial magnetic phases observed in so-called type-II multiferroic materials, such as the delafossite oxide CuCrO$_2$, have drawn extensive attention due to their interesting physics and potential applications [1–6]. Specifically, the magnetic Cr$^{3+}$ ions (having a quasiclassical $S = 3/2$ spin) in CuCrO$_2$ form a triangular lattice on the $ab$ plane, and the compound exhibits an incommensurate properscrew spiral state (ICY state) below the critical temperature $T_N$. In this state, the spiral plane is perpendicular to the $ab$ layer, and the three spins in each triangle sublattice form the so-called $120^\circ$ structure as shown in Fig. 1(a). Interestingly, an electric polarization ($P$) along the spiral propagation vector $k$ is induced through the variation of the hybridization between the Cr $d$ orbitals and the O $p$ orbitals caused by spin-orbit coupling [6,7].

Owing to the strong magnetoelectric coupling in this system, a significant dependence of $P$ on the magnetic-field $H$ has been observed in experiments [8–10]. For example, the flop of $P$ from the $x$ axis to the $y$ axis has been reported due to the $90^\circ$ rotation of the spin–spiral plane under $H$ applied along the $y$ direction [11]. Theoretically, several $H$-induced cycloidal spiral phases have been uncovered in the anisotropic classical spin model for CuCrO$_2$ [12,13], well consistent with the experimentally reported electric polarization based on Arima’s mechanism for multiferroic behavior [7]. The competitions among magnetic frustration, Zeeman energy, and thermal fluctuations are suggested to be responsible for the changes in magnetoelectric properties in CuCrO$_2$ under $H$ [13].

On the other hand, the magnetic states of CuCrO$_2$ can also be effectively modulated through impurity doping, and several interesting phenomena have been reported in experiments [14]. For example, a spin glass state induced by the V$^{3+}$ for Cr$^{3+}$ substitution has been observed in the CuCr$_{1-x}$V$_x$O$_2$ series for $x > 0.18$ [15,16]. Similarly, a short-range antiferromagnetic (AFM) excitation resulted from the enhancement of a spin glass component has been observed in nonmagnetic Al-doped systems [17]. More interestingly, significant hole-doping effects have been uncovered in CuCr$_{1-x}$Mg$_x$O$_2$ for $x \leq 0.03$. In detail, $T_N$ shifts toward high $T$ with the substitution of nonmagnetic Mg$^{2+}$ for Cr$^{3+}$, indicating the important role of the coupling between the itinerant hole and the localized spin [18–21].

The study on the doping effects on magnetic states in multiferroic oxides becomes very important from the following two viewpoints. On one hand, this study helps one to understand the multiferroic physics and to search for more attractive systems with improved magnetoelectric performance. On the other hand, despite the long history of research, spin glass phase transition is still a hot topic in statistical mechanics, whereas few results have been reported on triangular antiferromagnets [22]. Thus, the study of doped CuCrO$_2$ is essential both in application potential and in basic physical research. However, several doping effects on magnetic phase transitions reported in experiments are still far from well understood in theory, including: (1) spin glass behaviors reported in CuCr$_{1-x}$V$_x$O$_2$ and CuCr$_{1-x}$Al$_x$O$_2$ and (2) the unconventional promotion of the ICY state by the hole doping for the Mg substitution.

Fortunately, the earlier spin model for CuCrO$_2$ which has been successfully used to explain the magnetic-field effects allows one to explore the doping effects based on a modified model [13]. For example, in our earlier work, both the lattice defects and the random exchange induced by the isovalent substitution of nonmagnetic Al$^{3+}$ for Cr$^{3+}$ are confirmed to be responsible for the decrease in $T_N$ with the increasing Al-doping magnitude [23,24]. In this paper, we study the modified spin models to further investigate the doping effects on the magnetic phase transitions in doped CuCrO$_2$. Several experimental observations are well explained in our Monte Carlo simulations. In detail, it is suggested that: (1) the spin glass state in CuCr$_{1-x}$V$_x$O$_2$ is resulted from the competitions between the AFM Cr$^{3+}$–Cr$^{3+}$ coupling and the ferromagnetic (FM) V$^{3+}$–Cr$^{3+}$ coupling, and (2) the hole doping by Mg$^{2+}$ for Cr$^{3+}$ enhances the quantum fluctuations and bond disorder and modulates the biquadratic interactions and in turn enhances the ICY state.
FIG. 1. Spin structure and exchange interaction in (a) a clean system and (b) a doped system. The blue/red dotted lines denote the AFM/FM exchanges, and the red circle is the V3 ion. The second term is the in-plane hard-axis anisotropy with coupling, and the Zeeman coupling, and FM Cr3+ cations are also produced due to the additional holes, and itinerant holes are produced by Mg2+ substitutions, enhancing the quantum fluctuations and bond disorder. In earlier works, it has been clearly proved that both AFM Cr3+-Cr3+ coupling, weak AFM V3+.-V3+ coupling, and FM Cr3+-V3+ coupling as depicted in Fig. 1(b) [16]. Taking into account this fact, we studied a modified spin model for V3+ randomly doped CuCrO2, and the Hamiltonian can be written as

\[ H = \sum_{(i,j)} J_{ij} \Delta_{ij} S_i \cdot S_j + \sum_i \frac{1}{2} A_i S_i^2 - \sum_i \frac{1}{2} A_x S_i^2 - \sum_i H \cdot S_i, \]

where \( \Delta_{ij} \) is the exchange interaction between the nearest neighbors, and a spatial anisotropy with \( J'/J = 0.7654 \) is considered as shown in Fig. 1(a). The couplings between different ions are modulated by the parameter \( \Delta_{ij} \), which are chosen to be consistent with the experimental report. The second term is the in-plane hard-axis anisotropy with \( A_x = 0.005J \), the third term is the out-of-plane easy-axis anisotropy with \( A_z = 0.05J \), and the last term is the Zeeman coupling. Here, \( J'/J, A_z \) and \( A_x \) are chosen to be the same as those in earlier work [13], which well reproduce the spin state under zero \( H \). For simplicity, the length of \( S \) (Cr3+ and V3+), \( J \), and the Boltzmann constant are set to unity.

Several parameters are calculated in order to characterize the ICY state and spin glass state. For example, the vector chirality is calculated by [25]

\[ \chi = \frac{2}{3\sqrt{3}} N \sum_r (S_A \times S_B + S_B \times S_C + S_C \times S_A), \]

where \( N = L \times L \) is the amount of the total spins and the sum is over all the plaquettes of the system (ABC in Fig. 1). The components parallel \( (\chi_{||}) \) and perpendicular \( (\chi_{\perp}) \) to \( H \) or to the easy \( z \) axis \( (H = 0) \) are calculated. For the ICY state, \( \chi_{||} > 0 \) and \( \chi_{\perp} = 0 \) are expected. For the spin glass transition, the order parameter generalized to wave vector \( k \) is defined to be as follows:

\[ q^{\mu\nu}(k) = N^{-1} \sum_{\alpha} [q^{\alpha\mu}(k)^2]_{\alpha\nu}, \]

where \( q^{\mu\nu}(k) \) denotes the thermal average and \( [\cdots]_{\alpha\nu} \) is the average over disorder. In this paper, disorder averages are taken over \( N_k \) samples with \( N_k \) ranging from 400 for \( L = 6 \) to \( N_k = 10 \) for \( L = 24 \). Subsequently, the spin glass correlation length is determined from

\[ \xi_L = \left( \frac{1}{2} \sin(k_{\min}/2) \right)^{-1/2}, \]

where \( k_{\min} = (2\pi/L)(1,0,0) \). Thus, the freezing temperature \( T_g \) is estimated from the crossing points of \( \xi_L(L) \) for different \( L \)'s, according to the scaling law \( \xi_L/L = f[L^{1/\nu}(T - T_g)] \), where \( \nu \) is the correlation length exponent.

On the other hand, itinerant holes are produced by Mg2+ for Cr3+ substitutions, enhancing the quantum fluctuations and bond disorder. In earlier works, it has been clearly proved that thermal fluctuations and bond disorder can produce an effective biquadratic exchange in the classical Heisenberg triangular antiferromagnet [28]. Furthermore, quantum fluctuations can also generate a similar term as uncovered by the perturbation theory in earlier work [29]. Thus, the biquadratic interactions are further taken into account in the model to study the Mg2+ doping effects,

\[ H_K = K_1 \sum_{(i,j)} (S_i S_j)^2 + K_2 \sum_{[i,k]} (S_i S_k)^2. \]

Here, the nearest-neighbor and the next-nearest-neighbor biquadratic interactions are considered. Furthermore, Cr3+ cations are also produced due to the additional holes, and a double-exchange FM interaction between Cr4+-Cr3+ may be available [21]. In this paper, we set \( \Delta_z = -1 \) for the Cr4+-Cr3+ interaction and neglect the lattice defects and the itinerancy of Cr4+ due to the very small amount of Mg2+.

Our simulation is performed using the standard Metropolis algorithm and temperature-exchange method [30,31]. Unless stated elsewhere, the simulation is performed on a \( 24 \times 24 \) lattice with periodic boundary conditions.
III. SIMULATION RESULTS AND DISCUSSION

A. Spin glass state induced by magnetic/nonmagnetic impurity doping

First, we study the effects of the V doping on the magnetic properties in CuCrO$_2$. Figure 2(a) shows the simulated $\chi_{\perp}$ as a function of $T$ for various $x$’s. In the clean limit $x = 0$ when $T$ falls down to the transition point, $\chi_{\perp}$ increases, whereas $\chi_{\parallel}$ and the spin coplanarity remain small (not shown here), figuring the development of the ICY state. With the increase in $x$, the $\chi_{\perp}$ curve shifts toward the low-$T$ side, demonstrating the suppression of the ICY state. The transition point $T_N$ ($T_{\text{peak}}$, exactly) can be roughly estimated from the position of the peak in the calculated specific heat $C$ as given in Fig. 2(b). It is clearly shown that $T_{\text{peak}}$ decreases with the increasing $x$, consistent with the experimental report [16]. Furthermore, the value of $\chi_{\perp}$ is also significantly decreased, indicating that the ICY state is not dominated at low $T$ (for $x > 0.2$, at least).

Interestingly, spin glass order at low $T$ emerges due to the combination of disorder and frustration for $x > 0.2$. For example, Fig. 3(a) shows the calculated $\xi_L/L$ as a function of $T$ for various $L$’s at $x = 0.5$. From the common well-defined crossing point, we estimate the freezing temperature $T_g = 0.087 \pm 0.003$. Actually, the finite temperature spin glass transition has been reported in a dilute Ising system on the triangular lattice [22]. In this paper, it is suggested that the V doping produces disorder and leads to spin glass behavior in the frustrated Heisenberg model with the uniaxial anisotropy [32]. Furthermore, we plot $\xi_L/L$ in the scaling form in Fig. 3(b) and estimate that the spin glass transition is with a critical exponent $\nu = 1.25 \pm 0.03$.

As a short summary, the simulated phase diagram for V doping is presented in Fig. 4(a) which qualitatively reproduces the experimental one. The conventional ICY state is suppressed with the increase in $x$, and a spin glass state is favored beyond $x > 0.2$ due to the introduction of disorder. Furthermore, the spatial anisotropy may be changed with $x$ in real materials. Thus, the case of the spatial isotropic model ($J' = J$) is also investigated, and the corresponding results are shown in Fig. 4(b). It is noted that the frustration is further enhanced in the model for $J' = J$ in favor of spin glass magnetism, resulting in the enlargement of the spin glass phase in the phase diagram. However, the estimated $\nu$’s for $x < 0.2$ are rather abnormal ($\nu > 2$), indicating that the spin glass behavior is a little different from that for $x > 0.2$. Furthermore, the calculated $\chi_{\perp}$ curves show that the ICY state can be well stabilized at low $T$ for $x < 0.2$ (the corresponding results are not shown here), further demonstrating that the estimated $T_g$ in this $x$ region is not a genuine one and additional disorder is needed for the development of the spin glass state.

On the other hand, it has been experimentally reported that the spin defects produced by Al doping destabilize the ICY state accompanying the enhancement of the spin glass component [17]. This behavior is also reproduced in our simulations in which the nonmagnetic Al$^{3+}$ impurity is simply considered as a lattice defect. The spin glass order can be observed at low $T$ when $x$ increases above 0.35 as shown in Fig. 5(a). Similarly, the case of $J' = J$ is also investigated, and a rough phase diagram on the ($x,T$)
FIG. 5. The estimated phase diagram on the \((x,T)\) plane for Al doping with (a) spatial anisotropy and (b) isotropy. The phase boundaries are also depicted.

B. Enhanced ICY state in a Mg-doped system

At first glance, the introduction of the lattice defects and FM \(\text{Cr}^{4+}\text{Cr}^{3+}\) interaction by the substitution of nonmagnetic Mg for Cr will definitely destabilize the ICY state, contrary to the experimental observation. Thus, the nontrivial promotion of the ICY state in Mg-doped CuCrO\(_2\) indicates the essential role of the doped holes in modulating the magnetic phase transition. It is expected that the interaction between the doped hole and the localized spin may enhance the quantum fluctuations which could be described by the classical biquadratic interactions [shown in Eq. (5)] [25]. Here, we introduce the additional biquadratic interactions in the model to study the hole-doping effects. Furthermore, in one of the earlier theoretical works studying a similar triangular antiferromagnet, it has been proved that quantum fluctuations may produce an effective biquadratic exchange (negative \(K_1\) and \(K_2\)), whereas bond disorder may generate a positive \(K_1\) interaction [28]. However, the exact values of \(K_1\) and \(K_2\) are not available so far, and we systematically studied the effects of \(K_1\) and \(K_2\) on the multiferroic phase transition in this paper.

Figure 6(a) shows the calculated specific heat curves for various \((K_1, K_2)\)'s. As the magnitude of the negative \(K_2\) increases from zero \((- K_2 < 0.08)\), the transition to the ICY state shifts toward the high-\(T\) side. It is easily noted that the ICY state can be further stabilized by the negative \(K_2\) interactions due to the fact that the angle between the next-nearest neighbors is much less than \(\pi/2\). The simulated results are summarized in Fig. 6(b) which presents the detailed phase diagram on the \((K_1, K_2)\) plane. Considering the small amount of Mg doping in experiments, the effective biquadratic exchanges are expected to be much weaker than the spin exchanges. Thus, it is strongly suggested that the cooperation of the enhanced quantum fluctuations and bond disorder may cover the negative effect of the FM \(\text{Cr}^{4+}\text{Cr}^{3+}\) interaction and enhance the ICY state, leading to the increase in \(T_{\text{peak}}\), qualitatively consistent with experimental observation [19].

Furthermore, earlier experiments reveal that \(T_{\text{peak}}\) for \(x = 0.03\) shifts toward low \(T\) by applying a 9-T magnetic field,
whereas that for \( x = 0 \) is almost unaffected, demonstrating improved magnetoelectric properties in the Mg-doped system [19]. This interesting phenomenon is also captured in our simulations, and the calculated results are shown in Fig. 7 which well reproduces the experimental observations. In the clean limit \( x = 0 \), the specific heat curves for \( H_y = 0 \) and \( H_y = 0.3 \) (magnetic field applied along the y axis) coincide with each other [Fig. 7(a)], indicating that \( H_y = 0.3 \) never affects the AFM transition behavior. For \( x = 0.03 \), \( T_N \) shifts toward the low-\( T \) side, and the peak height of \( C \) is noticeably decreased by applying \( H_y = 0.3 \). Thus, it is strongly suggested that the FM Cr\(^{3+}\)-Cr\(^{3+}\) interaction and biquadratic exchanges induced by Mg\(^{2+}\) doping are responsible for the magnetic-field effects on \( T_{\text{peak}} \) in the hole-doped CuCrO\(_2\).

IV. CONCLUSION

In conclusion, we have studied the doping effects on the magnetic states of CuCrO\(_2\) by the Monte Carlo simulation of the frustrated spin models. It is suggested that the disorder induced by V/Al doping and the frustration in the system may result in the emergence of the spin glass state, consistent with the experimental observations. Furthermore, the hole doping by Mg\(^{2+}\) substituting Cr\(^{3+}\) enhances the quantum fluctuations and bond disorder and in turn leads to the unconventional promotion of the AFM ICY state.

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