


# Conical order, magnetic compensation, and sign reversible exchange bias in spinel structured $AB_2O_4$ compounds: A Monte Carlo study

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$AB_2O_4$  are a special class of spinel structured compounds exhibiting unique multiferroic properties. Recent experimental observation confirms switchable polarization in  $ACr_2O_4$  ( $A = \text{Co, Mn, Fe}$ ), arising out of non-collinear magnetic spin order. In this paper we unfold the microscopic origin behind such magnetic spin order, hysteresis, polarization, and the so-called magnetic compensation effect in  $ACr_2O_4$  ( $A = \text{Co, Mn, Fe, Ni}$ ) using Monte Carlo simulation. We have carefully constructed a set of exchange interaction parameters, which help to explain various experimental findings such as magnetization vs temperature ( $T$ ), conical stability, magnetic ordering, and polarization in a representative compound  $CoCr_2O_4$ . When substituted with Fe,  $CoCr_2O_4$  shows few exotic phenomena such as sign reversible exchange bias effect and magnetic compensation.  $CoMn_2O_4$  and  $CoFe_2O_4$  are two other compounds in the spinel family where we found no conical spin order and polarization, and thus facilitate a distinct contrast compared to others.

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## I. INTRODUCTION

$CoCr_2O_4$  is a classic example of spinel which is observed to show a new kind of polarization at very low temperature, whose origin lies in the formation of a conical magnetic order [1]. The application of the magnetic field manipulates the cone angle and hence the coupling between ferromagnetism and ferroelectric properties. Similar multiferroism has been reported for other spinel compounds such as  $MnCr_2O_4$  [2],  $FeCr_2O_4$  [3], and  $NiCr_2O_4$  [4]. These four spinels possess both polarization and magnetism due to spin origin. However, there are several other compounds,  $RMnO_3$  ( $R = \text{Tb, Dy}$ ), in the perovskite family where the polarization is due to spin-spiral developed in the plane [5,6]. Therefore, such a compound does not have any net magnetization ( $M$ ). However, the conical magnetic order in  $ACr_2O_4$  adds an extra magnetism along the cone axis and makes these compounds much more interesting.

There have been some experiments on this class of  $AB_2O_4$  compounds, which provide useful information about their novel properties. Yamasaki *et al.* [1] reported the signature of polarization in  $CoCr_2O_4$  below  $T_s = 27$  K. They also showed how polarization can be controlled using magnetic field. Neutron scattering experiments on  $ACr_2O_4$  ( $A = \text{Co, Mn}$ ) was first performed by Tomiyasu *et al.* [2], who estimated the cone angle by analyzing the experimental intensity of satellite reflections. They also proposed a unique concept of “weak magnetic geometrical frustration” (MGF) in spinel  $AB_2O_4$ , where both  $A$  and  $B$  cations are magnetic. Such weak MGF is responsible for the short-range conical spiral. Using neutron diffraction, Chang *et al.* [7] predicted a transformation from

incommensurate conical spin order to commensurate order in  $CoCr_2O_4$  at lowest temperature. A complete understanding of such transformation is lacking in the literature. Spin current model [8] is one simplistic approach which provides some conceptual advancement about incommensurate conical spin order, however, a firm understanding of incommensurate to commensurate transformation requires a better model.

These classes of compounds show a few other phenomena such as negative magnetization, magnetic compensation, and sign reversible exchange bias at a critical temperature called magnetic compensation temperature ( $T_{\text{comp}}$ ) [9–14]. This is a temperature at which different sublattice magnetization cancels each other to fully compensate the net magnetization ( $M = 0$ ). Interestingly, it changes sign if one goes beyond this temperature. Depending on the substituting element, in some cases, magnetic compensation is associated with the exchange bias phenomena. Such unique phenomena are very useful for magnetic storage devices which require a reference fixed magnetization direction in space for switching magnetic field. Compounds having exchange bias are highly suitable for such a device because their hysteresis is not centered at  $M = 0$ ,  $H = 0$ , rather shifted towards  $+ve$  or  $-ve$  side. Although the phenomena of exchange bias are well understood in various compounds including FM/AFM layered compounds [15], the same is not true for the substituted spinel compounds which crystallize in a single phase. A deeper understanding of all these exotic phenomena is highly desired.

Using the generalized Luttinger-Tisza [16] method, a conical ground state can be found theoretically [17] by defining an empirical parameter  $u$ ,

$$u = \frac{4J_{BB}S_B}{3J_{AB}S_A},$$

where  $S_A$  and  $S_B$  are the  $A$ -site (tetrahedral) and  $B$ -site (octahedral) magnetic spins,  $J_{AB}$  and  $J_{BB}$  represent the exchange

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interaction between first nearest neighbor  $A$ - $B$  and  $B$ - $B$  pairs, respectively. According to the theory, the stable conical spin order is possible only if  $u$  lies between 0.88 and 1.30. This is just a suggestive model to ensure the stability of conical spin order. Yan *et al.* [18–23] have studied the conical spin order by performing simulation on a three-dimensional spinel lattice. They show that  $\hat{J}_{BB}$  and  $\hat{J}_{AA}$  enhance the spin frustration, and single ion anisotropy helps to stabilize the cone state. Here  $\hat{J}_{ij} = J_{ij} |\vec{S}_i| \cdot |\vec{S}_j|$  and is called the magnetic coupling constant.

In this article the conical spin order of  $ACr_2O_4$  ( $A = Mn, Fe, Co,$  and  $Ni$ ) along with  $CoMn_2O_4$  and  $CoFe_2O_4$  are studied using Monte Carlo simulation. The later two compounds do not show conical spin order. We have varied the interaction parameters and found a suitable set of exchange interactions which best reproduce the experimental magnetic ground state and magnetization vs  $T$  curve. We have also simulated the hysteresis curve and exchange bias behavior. We found an effective exchange interaction for the system  $CoCr_2O_4$ , for which its magnetization is similar to  $Fe$  substituted  $CoCr_2O_4$  showing a magnetic compensation effect. Using these sets of exchange interactions, we are able to predict the sign reversible exchange bias at around  $T_{comp}$ , as observed experimentally [9].

## II. METHODOLOGY

For calculation, we have generated a three-dimensional spinel structure involving a  $7 \times 7 \times 7$  supercell of 2 formula unit which contains a total of 2058 numbers of magnetic atoms. Oxygen atoms are removed while generating the supercell as they do not contribute to magnetization. We defined the energy equation as

$$E = - \sum_{(i,j)} J_{ij} \vec{S}_i \cdot \vec{S}_j - \vec{M} \cdot \vec{h}_m - \vec{P} \cdot \vec{h}_e, \quad (1)$$

where  $\vec{P}$  and  $\vec{M}$  are polarization and magnetization, respectively, defined as

$$\vec{P} = a \sum_{(i,j)} \vec{e}_{ij} \times \vec{S}_i \times \vec{S}_j \quad (2)$$

and

$$\vec{M} = \sum_i g\mu_B \vec{S}_i, \quad (3)$$

where  $\vec{e}_{ij}$  is the vector connecting  $\vec{S}_i$  and  $\vec{S}_j$ ,  $a$  is a proportionality constant, and  $g$  is the Landé  $g$  factor whose value is taken to be 2.  $\vec{h}_m$  and  $\vec{h}_e$  are the applied magnetic and electric field. We solve this energy equation by Monte Carlo simulation where the spins are considered as classical vectors that are updated by the Metropolis algorithm keeping a periodic boundary condition on the cell. 1 00 000 steps are taken for equilibration and the average of the last 5000 steps data are used to calculate physical quantities.  $\sum_{(i,j)}$  is summation over nearest  $B$ - $B$ ,  $A$ - $B$ , and  $A$ - $A$  type of neighbors, while the higher-order neighbors are neglected. For the calculation of temperature dependence of magnetization, we have taken 5000 Monte Carlo steps for each temperature and the temperature is increased in steps of 1 K. To reach the correct

conical ground state, we have applied a large electric field (20 000 kV/m along [110] directions) and a magnetic field (20 T along [001] direction). Such huge fields were applied only to create/initiate a conical spin-spiral at the beginning of our calculations. Once the spin-spiral gets developed, we switch off both the magnetic as well as the electric field for the rest of our calculation. As such, these huge magnetic/electric fields are not the operative fields at which the actual magnetic properties are simulated. Such a procedure for the initial creation of conical spin-spiral has been used routinely in various reported literature in the past [18–23].

To check the size effect, we have also done the calculation for larger sized cells such as  $8 \times 8 \times 8$  (3072 atoms),  $10 \times 10 \times 10$  (6000 atoms), and  $12 \times 12 \times 12$  (10 368 atoms) supercells. The key magnetic properties such as magnetization, transition temperature, etc., however, do not change much beyond 2058 atoms results. As such, the rest of the calculations are done using  $7 \times 7 \times 7$  supercells only.

## III. RESULT AND DISCUSSION

### A. Exchange interaction parameters and magnetization

In order to perform the Monte Carlo simulation for various magnetic properties, we have chosen a set of exchange interaction parameters which best fits the experimental magnetic ground state. It is to be noted that our chosen parameters are short ranged (near neighbors only) in nature. The higher neighbor interactions in our calculations are captured within a mean-field scheme. We have also obtained these interaction parameters ( $J_{ij}$ ) from self-consistent DFT calculations (labeled as set-1), and simulated the magnetic properties of the said compounds. These results are shown in the Supplemental Material [24]. Apparently the magnetic properties simulated using these parameters compare less well with experiment than the fitted ones. Table I shows the fitted exchange interaction parameters ( $J_{ij}$ ), conical spin order parameters ( $u$ ), magnetic moments at  $A$  and  $B$  sites, and ferrimagnetic to paramagnetic transition temperature ( $T_c$ ) for the six  $AB_2O_4$  spinel compounds. These interaction parameters are chosen in such a way to reproduce the experimental magnetic ground state and  $M$  vs  $T$  curve. For  $CoMn_2O_4$ , the Mn-Mn bond lengths in the  $xy$  plane are smaller as compared to those which are out-of-plane. This gives rise to a stronger interaction for the former as compared to later. I and O represent the in-plane and out-of-plane  $\hat{J}_{BB}$  interaction parameters for  $CoMn_2O_4$ . For  $CoFe_2O_4$ , which crystallizes in inverse spinel structure, half of the  $B$  site are filled with Co and the rest by Fe. This geometry creates three types of  $B$ - $B$  interactions (Co-Co, Fe-Fe, and Co-Fe) and two types of  $A$ - $B$  interactions (Fe-Co and Fe-Fe).

Figure 1 shows a comparison of theoretical and experimental temperature dependence of magnetization for six compounds. The red line indicates the calculated magnetization while the solid plus symbols show the experimental data, wherever available. It is to be noted that, for our main compound  $CoCr_2O_4$ , the calculated magnetization using exchange interactions matches fairly well with those of experimental data [9].

TABLE I. For six  $AB_2O_4$  spinel compounds, coupling constants ( $\hat{J}_{BB}$ ,  $\hat{J}_{AB}$ , and  $\hat{J}_{AA}$ ), conical spin order parameter ( $u$ ), spin values at each sites ( $S_A$  and  $S_B$ ) used in MC simulation, and simulated and experimental ferrimagnetic to paramagnetic transition temperature ( $T_c$ ). For  $CoMn_2O_4$ , the Mn-Mn bond lengths in the  $xy$  plane are smaller compared to those out-of-plane, making the interaction much stronger for the former. These interaction parameters are labeled by I and O. For  $CoFe_2O_4$ , which crystallizes in an inverse spinel structure, half of  $B$  site are filled with Co and the other half by Fe,  $A$  sites are completely filled by Fe. This creates three types of  $B$ - $B$  interactions (Co-Co, Fe-Fe, and Co-Fe) and two types of  $A$ - $B$  interactions (Fe-Co and Fe-Fe).

System	Coupling constants			$u$	Spin		Calculated	Expt.
	$\hat{J}_{BB}$ (meV)	$\hat{J}_{AB}$ (meV)	$\hat{J}_{AA}$ (meV)		$S_A$	$S_B$	$T_c$ (K)	$T_c$ (K)
$MnCr_2O_4$	-0.97	-0.85	0.00	1.52	5/2	3/2	42	51 [2]
$FeCr_2O_4$	-1.38	-1.94	-0.67	0.95	4/2	3/2	103	74 [25]
$CoCr_2O_4$	-4.25	-2.83	0.00	2.00	3/2	3/2	94	97 [26]
$NiCr_2O_4$	-3.75	-2.38	0.00	2.10	1	3/2	80	80 [27]
$CoMn_2O_4$	-5.46 (I)	-3.53	-0.29	2.06	3/2	2	60	77 [28], 90 [29]
	-3.05 (O)			1.15	3/2	2		
$CoFe_2O_4$	0.08 (Co-Co)	-10.00 (Fe-Co)	-2.06	0.63	2	3/2 (Co), 2 (Fe)	840	860 [30]
	-4.77 (Fe-Fe)	-10.00 (Fe-Fe)						
	0.84 (FeCo)							

Table I also displays the stability parameter ( $u$ ) for all six compounds.  $u$  turn out to be 2.00 and 1.5 for  $CoCr_2O_4$  and  $MnCr_2O_4$  respectively.

For  $MnCr_2O_4$ , the  $u$  value lies beyond the stability range ( $0.88 < u < 1.3$ ). Interestingly the average  $\langle u \rangle$  calculated by Tomiyasu [2] using the neutron scattering data, within the generalized Luttinger-Tisza [16] method, for  $CoCr_2O_4$  and  $MnCr_2O_4$  are 2.00 and 1.50 which matches exactly with our calculated  $u$  values. In the case of  $NiCr_2O_4$ , the simulated

magnetization which best matches the experimental values require negligibly small  $\hat{J}_{AA}$  interactions, as in the previous two cases. We do not have any experimental magnetization data for  $FeCr_2O_4$ . We found that the choice of exchange interactions should be  $\hat{J}_{AB} > \hat{J}_{BB}$ , else it gives a magnetic compensation for  $FeCr_2O_4$ , which is only observed in substituted spinel compounds. The calculated  $u$  parameter for  $FeCr_2O_4$  is 0.95 which lies within the stability range. It should be noted that the Luttinger-Tisza model is a purely classical model in which the concerned expression only involves  $\hat{J}_{BB}$  and  $\hat{J}_{AB}$  interactions. In spite of the fact that the  $\hat{J}_{AA}$  interaction is vanishingly small for the first four (conical) spinel systems, the calculated  $u$  parameter for three systems falls beyond the stability range. This clearly indicates that this model may not provide accurate stability predictions for all systems and the given  $u$  parameter range ( $0.88 < u < 1.3$ ) is only suggestive.

The calculated magnetic transition temperature ( $T_c$ ) is also tabulated in Table I along with the experimental values for comparison.

It is to be noted that  $T_c$  for  $FeCr_2O_4$  is calculated to be 103 K, whereas the magnetization of different sublattices cancel each other out and compensate the net moments for temperature above 93 K. For  $CoMn_2O_4$ , the simulated  $M$  vs  $T$  curve does not compare well with the experimental data, nor does it show a sharp magnetic transition. To be precise, here the transition temperatures ( $T_c$ ) are estimated from the magnetization graph of individual ions (mainly the Mn atoms which dominantly contribute to magnetism in this system and hence play the key role in dictating  $T_c$ ). Figure 2 shows the atom projected magnetization ( $M$ ) vs  $T$  curve for  $CoMn_2O_4$ . The discrepancy between the calculated and experimental  $M$  vs  $T$  curve could be due to various reasons, e.g., (i) less number of equilibration loops and (ii) the antisite disorder involving Co and Mn atoms, as reported experimentally [28], the effect of which is not included in our present calculations

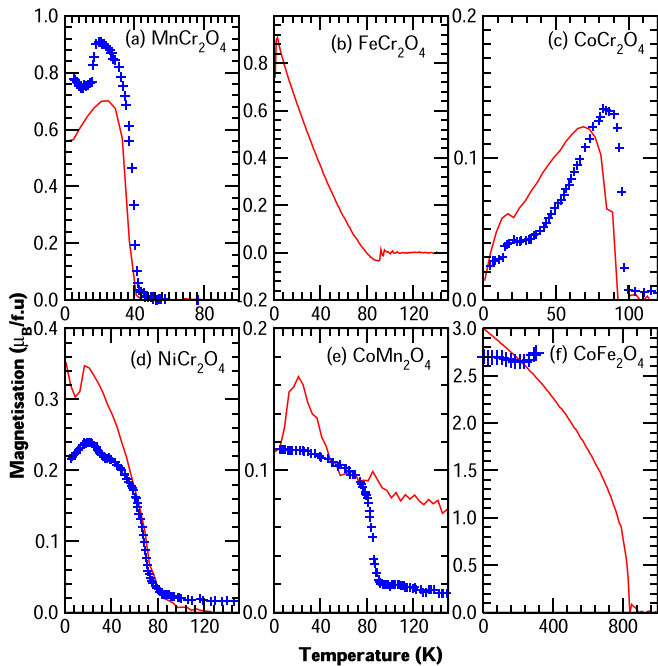


FIG. 1. Temperature dependence of magnetization for six spinel compounds  $AB_2O_4$ . Red line shows the calculated magnetization and plus (+) symbol indicates experimental data [4,28].

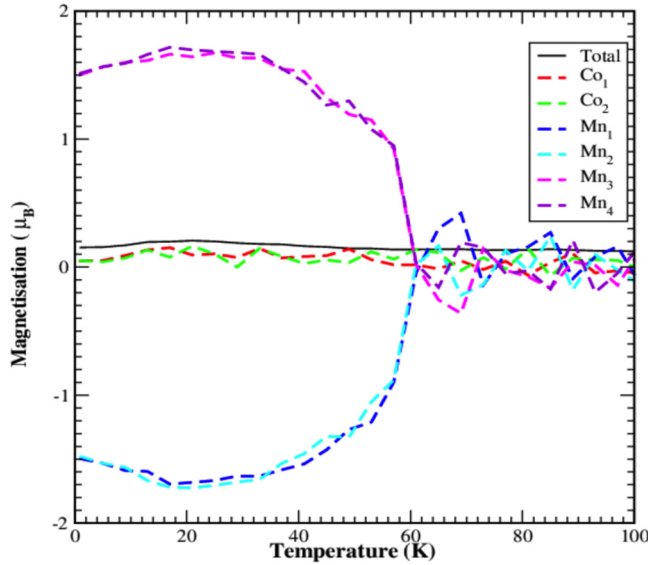


FIG. 2. Total and atom projected magnetization ( $M$ ) vs  $T$  for  $\text{CoMn}_2\text{O}_4$ . The transition temperature ( $T_c$ ) is evaluated from the Mn-projected  $M$  vs  $T$  curve, which is the dominant contributor of magnetism in this system.

### B. Magnetic order

Table II shows the calculated cone angle, types of spin order, polarization, and transition temperature ( $T_s$ ) for the six  $AB_2\text{O}_4$  compounds.  $T_s$  is the transition temperature above which a long-range spin-spiral chain breaks, as a result of which the polarization drops to zero. Experimental data are shown wherever available. There are three cone angles  $\theta_A$ ,  $\theta_{B_1}$ , and  $\theta_{B_2}$  based on sites  $A$ ,  $B_1$ , and  $B_2$ , respectively. The cone angles reported in Table II are the average values of  $\theta$  measured at the lowest temperature (0.01 K). Clearly the simulated value of the cone angles matches fairly well with those of experiments [2]. Four systems  $ACr_2O_4$  ( $A = \text{Mn}$ ,

Fe, Co, and Ni) show conical spin order, as also observed experimentally. As temperature increases, the average cone angle decreases and finally goes to zero. In addition, the polarization drops to zero at the same temperature  $T_s$  at which the conical magnetic order vanishes (i.e., the average conical angle becomes zero). For  $\text{CoMn}_2\text{O}_4$ , the vector corresponding to  $\theta_A$  is the resultant of those for  $\theta_{B_1}$  and  $\theta_{B_2}$ . In the case of  $\text{CoFe}_2\text{O}_4$ , however, the vector for  $\theta_A$  is antiparallel to those of  $\theta_{B_1}$  and  $\theta_{B_2}$ . These magnetic orderings are in fair agreement with the experimental observation [31].

We have also calculated the spin modulation vector from the ground state spin structure of one of the systems,  $\text{MnCr}_2\text{O}_4$ . This vector turns out to be  $\frac{2\pi}{a_0}(0.53, 0.53, 0)$ . The corresponding experimental value for this system is  $\frac{2\pi}{a_0}(0.59, 0.59, 0)$  [2].

### C. Compounds having no conical order: $\text{CoMn}_2\text{O}_4$ and $\text{CoFe}_2\text{O}_4$

From Table I, the first-principles calculated exchange interactions in  $\text{CoMn}_2\text{O}_4$  have a strong anisotropy because it crystallizes in a tetragonal structure, whereas all the other compounds are cubic. Due to stretching along the  $z$  direction and compression in the  $xy$  plane,  $\hat{J}_{BB}$  in the  $xy$  plane becomes much stronger and those out-of-plane turn weaker. In Table I, I and O refers to in-plane and out-of-plane interaction, respectively. Therefore at very low temperatures, all the spins lie in the  $xy$  plane and as temperature crosses  $T_c$ , they get completely randomized. For  $\text{CoFe}_2\text{O}_4$ , the ground state is collinear which corroborates the fact that  $\hat{J}_{AB}$  is much stronger than  $\hat{J}_{BB}$ . Interestingly, because this compound crystallizes in inverse spinel structure, which is not the case for the other five compounds, Fe sits at both  $A$  and  $B$  site with antiparallel alignment. This cancels out the magnetization from Fe and the observed magnetization is mostly due to the magnetic moment of collinear Co spins. Figure 3 shows a pictorial diagram of the calculated magnetic spin orders for all six compounds.

TABLE II. For the six compounds, calculated inclination angles ( $\theta_A$ ,  $\theta_{B_1}$ ,  $\theta_{B_2}$ ) of the ground state magnetic state, type of spin order, polarization, and conical transition temperature ( $T_s$ ). Here  $T_s$  is taken as the maximum temperature above which polarization of these compounds drops to zero. Experimental data are provided, wherever available.

System		Average inclination angle			Type of spin order	Polarization ( $\frac{\mu_C}{m^2}$ )	$T_s$ (K)
		$\theta_A$ (deg)	$\theta_{B_1}$ (deg)	$\theta_{B_2}$ (deg)			
$\text{MnCr}_2\text{O}_4$	Theor.	132	85	77	Conical	4.9	4
	Expt. [2]	152	95	11	Conical	–	16
$\text{FeCr}_2\text{O}_4$	Theor.	164	14	16	Conical	3.3	0
$\text{CoCr}_2\text{O}_4$	Theor.	142	83	40	Conical	1.8	16
	Expt. [2]	132	109	28	Conical	–	24
$\text{NiCr}_2\text{O}_4$	Theor.	144	84	37	Conical	0.9	17
$\text{CoMn}_2\text{O}_4$	Theor.	90	141	38	$A$ is the resultant of $B_1$ and $B_2$	0.1	0
	Expt. [31]	90	151	61	$A$ is the resultant of $B_1$ and $B_2$	–	0
$\text{CoFe}_2\text{O}_4$	Theor.	179	1	1	$A$ is antiparallel to $B_1$ and $B_2$	0.0	0
	Expt. [32]	180	0	0	$A$ is antiparallel to $B_1$ and $B_2$	–	0

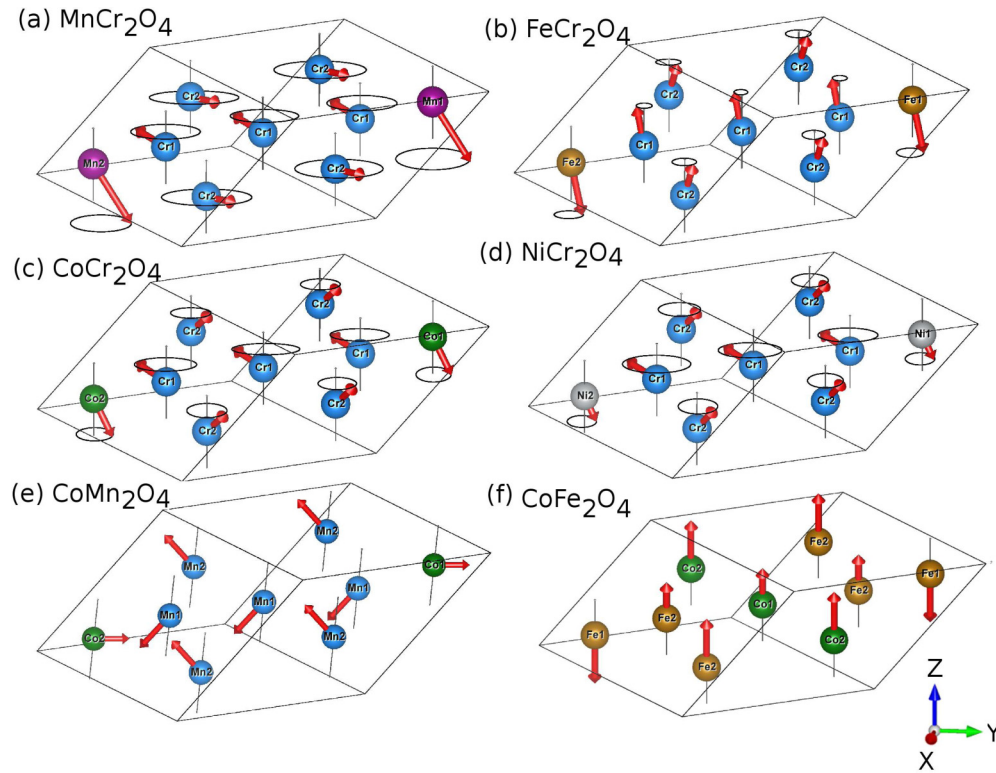


FIG. 3. The calculated magnetic order for six spinel compounds: (a)  $\text{MnCr}_2\text{O}_4$ , (b)  $\text{FeCr}_2\text{O}_4$ , (c)  $\text{CoCr}_2\text{O}_4$ , (d)  $\text{NiCr}_2\text{O}_4$ , (e)  $\text{CoMn}_2\text{O}_4$ , and (f)  $\text{CoFe}_2\text{O}_4$ .

#### D. Hysteresis

We have simulated the hysteresis curve for all six compounds using the fitted interaction parameters (see Table I). A comparative plot showing our simulated data and experimental curve is shown in Fig. S1 of the Supplemental Material [24]. One may ask a question, how can a simple Heisenberg Hamiltonian [such as Eq. (1)], with no explicit anisotropy term, yield a finite value of coercive field? Such an outcome is not new but has been reported in a number of literatures in the past [18,33,34]. One reason could be the finite sized supercells used in these simulations. Another reason can be the inherent anisotropy of the system itself. Although we have not included the anisotropy explicitly into our calculations, an inherent anisotropy is still present within the model due to the conical spin-spiral nature of the ground state  $\text{ACr}_2\text{O}_4$  compounds. As in the ground state, all the spins point in the shape of a cone with an inclination away from the  $z$  axis, one can realize an anisotropy along the  $z$  axis which unfavors the spins to align along this axis. On the other hand, in the case of systems such as  $\text{CoMn}_2\text{O}_4$ , there are two different sets of  $J_{BB}$  exchange interaction parameters [35] such that Mn atoms which interact with other Mn atoms located on the  $xy$  plane are nearly 10 times larger than the Mn atoms which are out of the  $xy$  plane. Such anisotropy in the exchange interactions also creates an inherent anisotropy.

#### E. Polarization

Polarization ( $P$ ) for  $\text{ACr}_2\text{O}_4$  is calculated using Eq. (2). The proportionality constant  $a$  is taken to be  $0.03 \frac{\mu\text{C}}{\text{m}^2}$ .  $P$  is calculated using the fitted interaction parameters, which

involve  $BB$ ,  $AB$ , and  $AA$  type of first neighbor interactions. Yao *et al.* [18–23] also reported the simulated polarization obtained using only the  $BB$ -type neighbor interactions. We observed that inclusion of  $AB$  and  $AA$  (in addition to  $BB$ ) interactions help us to achieve the stable conical spin-spiral order easily. Singh *et al.* measured the polarization for both  $\text{CoCr}_2\text{O}_4$  and  $\text{FeCr}_2\text{O}_4$  [3], and found the magnitude of  $P$  for  $\text{FeCr}_2\text{O}_4$  to be 10–12 times larger. This indicates that the choice of  $a$  value is crucial in the theoretical simulation of  $P$ . As we do not have much information for the rest of the compounds, for simplicity we have taken  $a$  to be  $0.03 \frac{\mu\text{C}}{\text{m}^2}$  for all the compounds. It is to be noted that as the magnitude of  $A$ -site spin decreases, the polarization also decreases. In  $\text{CoFe}_2\text{O}_4$ , the calculated polarization is nearly zero as all the spins are collinear. For the compound  $\text{CoMn}_2\text{O}_4$ , the simulated polarization is found to be quite small in magnitude,  $0.1 \frac{\mu\text{C}}{\text{m}^2}$ . The critical temperature  $T_s$  below which the polarization can be measured are also listed in Table II for all six compounds.

#### F. Magnetic compensation

It has been observed that some ferrimagnets have a critical temperature, below the ferrimagnetic-paramagnetic transition temperature ( $T_c$ ), called the magnetic compensation temperature ( $T_{\text{comp}}$ ), where the magnetization curve crosses the zero temperature axes. At  $T = T_{\text{comp}}$ , the antiferromagnetic spins of different sublattices are rearranged in such a way that they cancel each other out to give a compensating zero net magnetization. The magnetization just below and above  $T_{\text{comp}}$  have opposite signs. Such compensation has not been reported in any of the pristine spinel compounds  $\text{AB}_2\text{O}_4$ , but detected

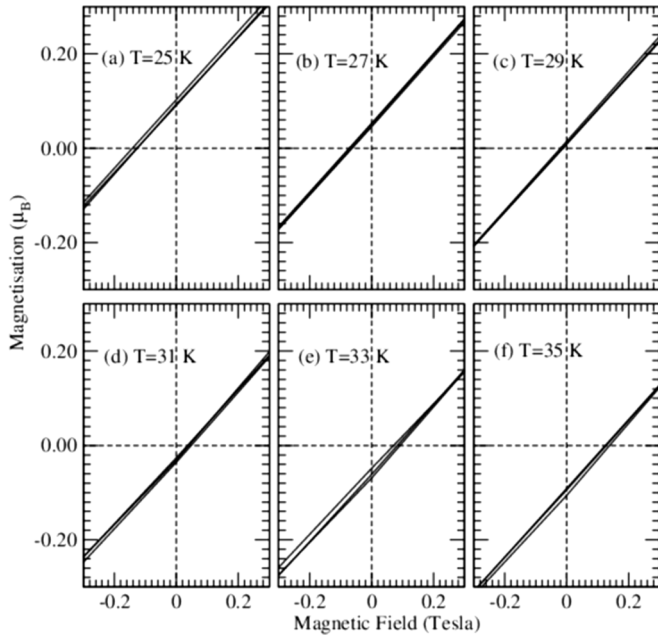


FIG. 4. Sign reversible exchange bias effect (shift of the origin of hysteresis with varying temperature) in  $\text{CoCr}_2\text{O}_4$  with  $\hat{J}_{BB}/\hat{J}_{AB} = 1.41$ .

in some of their substituted counterpart. It is not easy to simulate the substituted alloy systems, as we need to evaluate a new set of exchange parameters between the substituting magnetic atom and the rest of the atoms of the host compound. Also, the final results sensitively depend upon the substituting sites chosen in the Monte Carlo simulation. As such, we followed a different route and checked the possibility of magnetic compensation in the substituted systems by varying effective interaction parameter  $\hat{J}_{BB}/\hat{J}_{AB}$ . This is shown in Fig. S2 of the Supplemental Material [24]. The origin of magnetic compensation in  $AB_2O_4$  lies in the cancellation of magnetization between  $A$  and  $B$  sites which, in turn, depends on the exchange interactions. As such, the variation of atom projected magnetization with temperature can give helpful insights into the compensation mechanism. This is illustrated in detail for  $\text{CoCr}_2\text{O}_4$ , in Fig. S3 of the Supplemental Material [24], where total and atom projected magnetizations (on Co and Cr atoms) are shown.

### G. Exchange bias in $\text{CoCr}_2\text{O}_4$

Exchange bias is a phenomenon that shifts the origin of hysteresis on the magnetic axis. Most of the memory device and the devices based on spintronics application need a layer having exchange bias so as to fix the magnetic state with surrounding magnetic fluctuations. It has been reported that

very close to  $T_{\text{comp}}$ , exchange bias is observed in the Fe substituted  $\text{CoCr}_2\text{O}_4$  [9]. With a similar motivation as before, we have studied the appearance of exchange bias by mimicking the effect of substitution via the change in effective interactions. Figure 4 shows the shift in the hysteresis as a function of varying temperature with  $\hat{J}_{BB}/\hat{J}_{AB} = 1.41$  ( $\hat{J}_{BB} = -4.00$ ,  $\hat{J}_{AB} = -2.83$ ). These parameters can only be taken in an average sense representing the mean-field estimate of the exchange interactions for Fe-substituted  $\text{CoCr}_2\text{O}_4$ . Interestingly, at around 30.36 K, sign reversible exchange bias is observed. The transition temperature agrees fairly well with the magnetic compensation temperature, as observed experimentally [36]. A magnetostructural correlation has been observed at around  $T_{\text{comp}}$  in this compound [10,37,38]. The exchange bias arises mainly due to the magnetic spin order developed at low temperature.

## IV. CONCLUSION

In conclusion, we have used Monte Carlo simulation to study the possibility of conical magnetic spin order in a series of six  $AB_2O_4$  spinel compounds. A set of exchange interaction parameters are carefully constructed, which closely reproduce the experimental magnetization and the corresponding ground state magnetic ordering. These parameters are further used to evaluate several other magnetic properties such as polarization, hysteresis, exchange bias, etc.  $\text{CoCr}_2\text{O}_4$  is chosen as a representative system, for which we established the correct angle of conical order, as observed experimentally. The estimated transition temperature and polarization also agree fairly well with the experiment. We modeled the Fe substituted  $\text{CoCr}_2\text{O}_4$  using a different set of exchange interactions. These parameters can be considered as the effective interactions, within a mean-field sense, representing the alloy  $\text{Co}(\text{Cr}_{0.95}\text{Fe}_{0.05})_2\text{O}_4$ . As observed experimentally, this compound shows a sign reversible exchange bias effect at  $T_{\text{comp}} \simeq 30.4$  K. We have also simulated two other compounds,  $\text{CoMn}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$ , which turn out to show no conical magnetic order, as observed. The spin-current model used in our calculation works quite well for very low magnetic field. This model is also promising to predict the cone angle of the atomic spins and also explains the magnetic compensation and exchange bias phenomena.

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