# Steep energy landscapes and adjustable magnetization states in a four-layer mean-field model with competing interactions

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We present a mean-field model with competing interlayer interactions which give rise to organized frustration. The frustration arises due to the difference in modulation length of the interlayer exchange coupling in the mixed-spin state. We calculate the energy landscapes and the equations of state of the system and show how multiple configurations are possible. In addition, the study shows how in such a layered system with competing interactions magnetization jumps can occur at low temperature due to the sharp energy barriers in the landscape. Finally, we examine possible mechanisms of magnetization self-reversal via layer-moment switching.

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## I. INTRODUCTION

The energy balance in systems with competing interactions which generate frustration has been a topic of intense study in the past years.[1–6] In the context of frustrated magnetic materials a wide range of systems and concepts has been investigated. These include spin glasses,[7,8] spin liquids,[9,10] and sublattice-frustrated ferrimagnets.[11–13] The latter group represents a special class of materials, in which the competition is manifested between long-range-ordered sublattices. Moreover, mixed-spin ferrimagnets also exhibit compensation points[14–16] due to the different temperature dependence of the magnetic constituents.

An excellent example of this class of materials are members of the hemo-ilmenite solid solution series $(x)FeTiO_3$-$(1-x)Fe_2O_3$ with $x > 0.7$.[17–19] This system crystallizes in the $R\bar{3}$ symmetry,[20] where the Fe(II) and Ti(IV) cations are partitioned into consecutive A and B layers, respectively, and the Fe(III) ions are randomly distributed in all layers to compensate for charge imbalance. The cations are octahedrally coordinated with oxygen.[21] In this configuration both Fe ions are in the high-spin state, i.e., $3d^4$, $S = 4/2$ for Fe(II) and $3d^5$, $S = 5/2$ for Fe(III).[22,23] This setup generates Fe-rich (A) and Fe-deficient (B) alternating layers. Inside each layer, the spins of the Fe ions prefer parallel alignment due to direct exchange interactions,[24] but spins from neighboring layers show different behavior. Fe(II) spins in subsequent A layers in ilmenite order antiparallel to each other due to the oxygen-induced superexchange, and thus have a modulation of 4 crystalline layers;[23,25] Fe(III) spins, however, exhibit a modulation of 2 crystalline layers as in the end-member hematite.[26] Hence the system demonstrates layerwise frustration of the interactions due to the difference in modulation lengths along the $c$ axis which results in a freezing event at a finite temperature $T_f$.[17,19] This magnetic partitioning was recently verified by low-temperature magnetization loops, which exhibit multiple metamagnetic transitions attributed to collective layer rotation.[27] The layerwise frustration enables a detailed theoretical study of such a system, where the focus lies on the competition of the interlayer exchange coupling.

In this work we investigate a four-layer model system containing two A layers (major moment carriers) and two B layers (minor moment carriers) (see Fig. 1), where all layers interact with each other with competing interlayer exchange energies. The study, even though motivated by experimental observations, is purely theoretical and aims towards understanding the mechanisms of energy-balance competition in a virtual system with a finite number of degrees of freedom, i.e., the four layers. For this purpose, we compare two systems, one with composition $x = 1.0$, i.e., only A layers, and one with $x = 0.8$. The comparison between the two systems will elucidate the effect of the mixed modulation of interlayer exchange energies in the mixed-spin state.

## II. FOUR-LAYER MODEL

We model the magnetic unit cell of the system as a four-layer magnet containing A1, B1, A2, and B2 layers (Fig. 1). The interactions between the layers can be represented by three effective exchange constants: $J_{AA}$ for A1-A2, $J_{BB}$ for B1-B2, and $J_{AB}$ for A-B interactions. We assume that all spins within each layer are ordered parallel due to direct exchange, and thus the intralayer exchange energies are $J_A > 0$ for A layers and $J_B > 0$ for B layers. Considering the interaction modulation of Fe(II) and Fe(III) in the real system, A1 and A2 will tend to align antiparallel to each other ($J_{AA} < 0$, as in $FeTiO_3$), B1 and B2 will tend to align parallel to each other ($J_{BB} > 0$, as in $Fe_2O_3$), while the A's and B's will tend to align antiparallel to each other ($J_{AB} < 0$, as in $Fe_2O_3$). Therefore, from the three effective exchange constants in this geometry, only two of the interlayer bonds can be satisfied at any given time. For example, when A1-A2 are antiparallel and B1-B2 are parallel, $J_{AA}$ and $J_{BB}$ are satisfied but $J_{AB}$ is not [Fig. 1(a)]. In another scenario, when both A1-A2 and B1-B2 are parallel, the $J_{BB}$ and $J_{AB}$ are satisfied but the $J_{AA}$ is not [Fig. 1(b)]. In a more general sense, the four layers represent a system with four coupled degrees of freedom.

First, we construct a general Hamiltonian for a system with $K$ layers and then reduce it to the four layers. The Hamiltonian

 

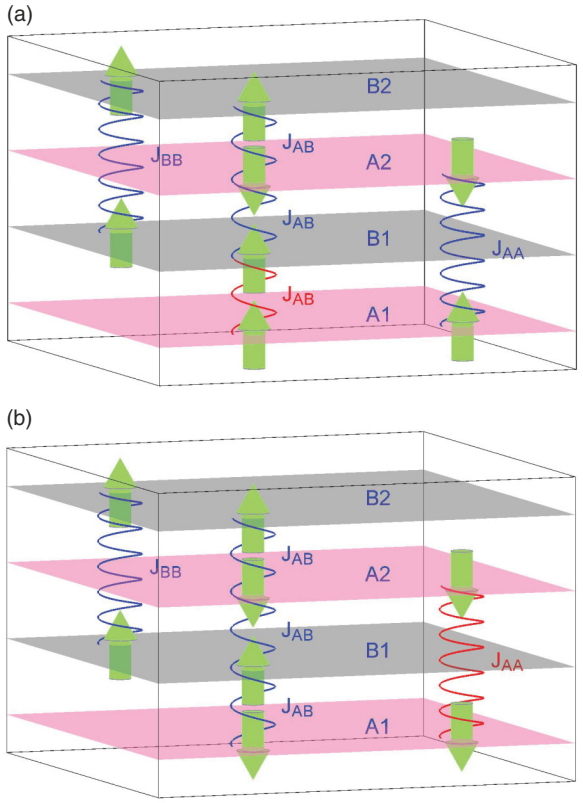


FIG. 1. (Color online) Illustration of the four-layer model with interlayer interactions $J_{AA}$, $J_{BB}$, and $J_{AB}$. The green arrows indicate the direction of the layer moment, blue spirals correspond to satisfied bonds, and red spirals to frustrated bonds between layers. Only two bonds can be satisfied at the same time. Example (a) shows a case where one of the $J_{AB}$ bonds is suppressed, and example (b) another case where the negative $J_{AA}$ is suppressed.

of the $k$th layer in the system can be written as

$$\mathcal{H}_k = -\frac{1}{2}\sum_{i}^{N_k}\left(\sum_{j}^{z_k} J_{k,ij}\,S_{k,i}\,S_{k,j} + \sum_{l\neq k}^{K-1}\sum_{j}^{z_{kl}} J_{kl,ij}\,S_{k,i}\,S_{l,j}\right) - \mu_B g h \sum_{i}^{N_k} S_{k,i}\,, \tag{1}$$

where $N_k$ is the number of atoms in layer $k$, $J_{k,ij}$ is the intralayer interaction in layer $k$, $S_{k,i}$ and $S_{k,j}$ are the interacting spins in layer $k$, $z_k$ is the number of interacting neighbors in layer $k$, $K$ is the total number of layers (in this case $K = 4$), $J_{kl,ij}$ is the interlayer interaction constant between spins $S_{k,i}$ and $S_{l,j}$, and $h$ is the external field. We consider Ising-type spins; i.e., the spins are all confined in one axis and $S = \pm|S|$, since hemo-ilmenite has been found to exhibit Ising-like behavior.[19,26] Moreover, in the Hamiltonian we assume that all spins interact with each other, i.e., that we have a uniform mean field.

We simplify the above Hamiltonian using a mean-field approximation for both intra- and interlayer exchange interactions, assuming uniform layer magnetization $m_k$. Further, we can estimate the relative layer moment using the ionic contents of each layer which depend on the composition of the solid solution and will be $[(5-x)/2]\mu_B$ for A's and $[5(1-x)/2]\mu_B$ for B's. For the discussion the layer moments are normalized to their relative value, i.e., $-1 \leqslant m_k \leqslant +1$. Finally, the mean-field Hamiltonian of the $k$th layer in the system reads

$$\mathcal{H}_k^{\mathrm{MFA}} = \underbrace{\frac{N_k}{2} z_k J_k m_k^2 + \sum_{l\neq k}^{K-1}\left(\frac{N_k}{2} z_{kl} J_{kl} m_k m_l\right)}_{X_k} - \underbrace{\left(z_k J_k m_k + \mu_B g h + \sum_{l\neq k}^{K-1} z_{kl} J_{kl} m_l\right)}_{Y_k}\sum_{i}^{N_k} S_{k,i}\,, \tag{2}$$

which now has the familiar form of

$$\mathcal{H}_k = X_k - Y_k \sum_{i}^{N_k} S_{k,i}\,, \tag{3}$$

where the spins are disentangled and this allows us to calculate the partition function of the canonical ensemble $Z(T)$. From this we calculate the energy density $F(T)_k$ for each sublattice:

$$\begin{aligned} F(T)_k &= -\frac{1}{\beta N_k}\ln Z(T)_k \\ &= -\frac{1}{\beta N_k}\ln\{e^{-\beta X_k}[2\cosh(|S_k|\beta Y_k)]^{N_k}\} \\ &= \frac{X_k}{N_k} - \frac{1}{\beta}\ln[2\cosh(|S_k|\beta Y_k)]\,, \end{aligned} \tag{4}$$

where $\beta = 1/k_B T$ is the inverse thermal energy at temperature $T$ with the Boltzmann constant $k_B$. The total energy density is then the sum of all four layer energies ($F_{\mathrm{tot}} = F_{A1} + F_{B1} + F_{A2} + F_{B2}$). Finally we arrive at the equations of state of the system, which have the form

$$m_k = -\left[\frac{\partial F(T)_k}{\partial h}\right]_h = |S_k|\,\mu_B g \tanh(|S_k|\,\beta Y_k)\,. \tag{5}$$

These equations are self-consistent; i.e., they have the form $m_k = f(m_k)$. Therefore, we calculate the deviation from the self-state as $E_k = m_k - f(m_k)$, whereas for the whole system it can be defined as

$$E = \sqrt{E_{A1}^2 + E_{B1}^2 + E_{A2}^2 + E_{B2}^2}. \tag{6}$$

Using Eqs. (6) and (4) we can calculate the state $E$ and the energy $F$ of the system, respectively, as a function of the individual layer moments, i.e., as a function of either the A or the B layers, at constant temperature. When calculating $E(m_{A1},m_{A2})$ and $F(m_{A1},m_{A2})$ we have to assume a constant configuration of the B layers and vice versa. By calculating the energy landscapes and the equations of state of the system as a function of the layer moments, we may locate the frustrated symmetries in the system and be able to predict the energy minima (global and local), as well as the mechanisms of layer-moment switching.

The energy-balance in the system is decided by the values of $J_{AA}$, $J_{AB}$, and $J_{BB}$. Considering that each spin has three nearest neighbors within the layer and one nearest neighbor in the neighboring layer, the intralayer exchange will be

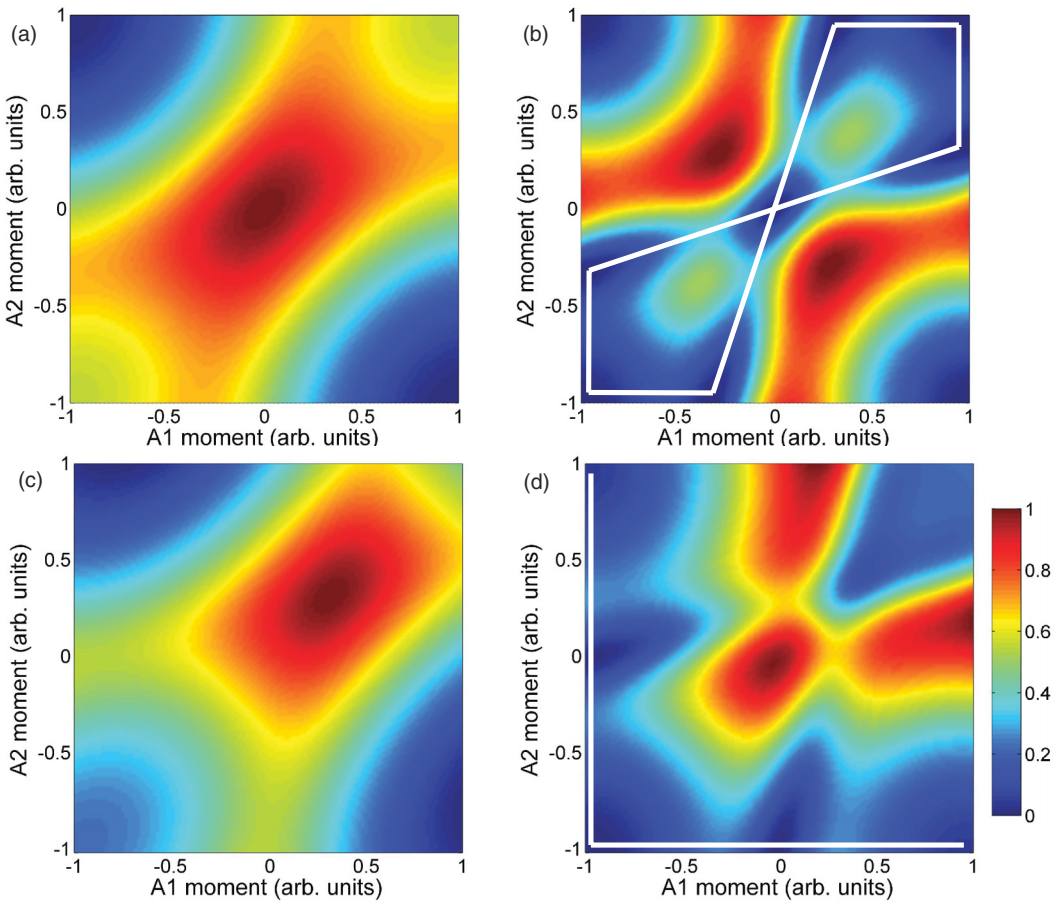


FIG. 2. (Color online) Energy landscapes (left) and equation of state (right) calculated using Eqs. (4) and (6), respectively, for compositions $x = 1.0$ [(a), (b)] and $x = 0.8$ [(c), (d)] as a function of A-layer moments at $T = 1 \times J_A$. The color bar on the right indicates the value of the normalized landscapes. The white lines in the right-hand panels indicate the possible movements of the system.

three times stronger. Moreover, taking into account the interion distances within the layers and between neighboring layers,[25] we may assume that interlayer interactions will be four times weaker than intralayer interactions. We therefore assign $|J_{AA}| = |J_{BB}| \approx |J_A|/4$, and $|J_{AB}| \approx |J_A|/2$. Since the occupancy of each layer is not the same, the contribution of the individual exchange constant to the total energy of the system is mediated via the layer moment, which is scaled to the occupancy. For simplicity, we scale all the exchange constants and the temperature to $J_A$ (=1) in the calculations.

## III. RESULTS AND DISCUSSION

As a first step, we calculate the energy landscape and the state of the system as a function of the A-layer moments at temperature $T = J_A$ for compositions $x = 1.0$ and 0.8 (see Fig. 2). In the case of $x = 1.0$, $m_{B1}$ and $m_{B2}$ are zero and do not have to be considered for the calculation. The system is described by a symmetric energy landscape and an equation of state which allows five A-layer configurations: $(m_{A1}, m_{A2}) = (0,0)$, $(1,1)$, $(1,-1)$, $(-1,1)$, and $(-1,-1)$. The energy landscape, however, has only two minima at $(1,-1)$ and $(-1,1)$, i.e., at antiparallel configuration of the layer moments. Therefore, the ground state of the system with $x = 1.0$ is clearly either $(1,-1)$ or $(-1,1)$. From the landscape of the equation of state [Fig. 2(b)] we can also determine the possible pathways of the layer moments in a case of switching from one state to another. As seen in the figure, at this temperature only switching between $(-1,-1)$ and $(1,1)$ via $(0,0)$ is possible. Such a switching, although it is allowed by the equation of state, can be excluded because it lies at the energy maxima as seen in Fig. 2(a).

For $x = 0.8$ the B-layer moments are nonzero and for the calculation they are assumed to be fixed at a parallel configuration. As seen in the figure [Figs. 2(c), 2(d)] the diagonal symmetry is lost and a new energy minimum is generated at $(-1,-1)$; i.e., the A-layer moments may be parallel to each other and antiparallel to the B-layer moments. From the landscape of the equation of state [Fig. 2(d)] we see that there is a pathway between the states $(1,-1)$, $(-1,-1)$, and $(-1,1)$. This suggests that upon application of an external field to the negative direction, the A-layer moments could be directed into a parallel configuration, antiparallel to the B-layer moments, and that the process would be reversible. If, however, a strong external field forces the A layers in a parallel positive configuration, i.e., $(1,1)$, which is allowed by the equation of state, then the system would be trapped in that local minimum

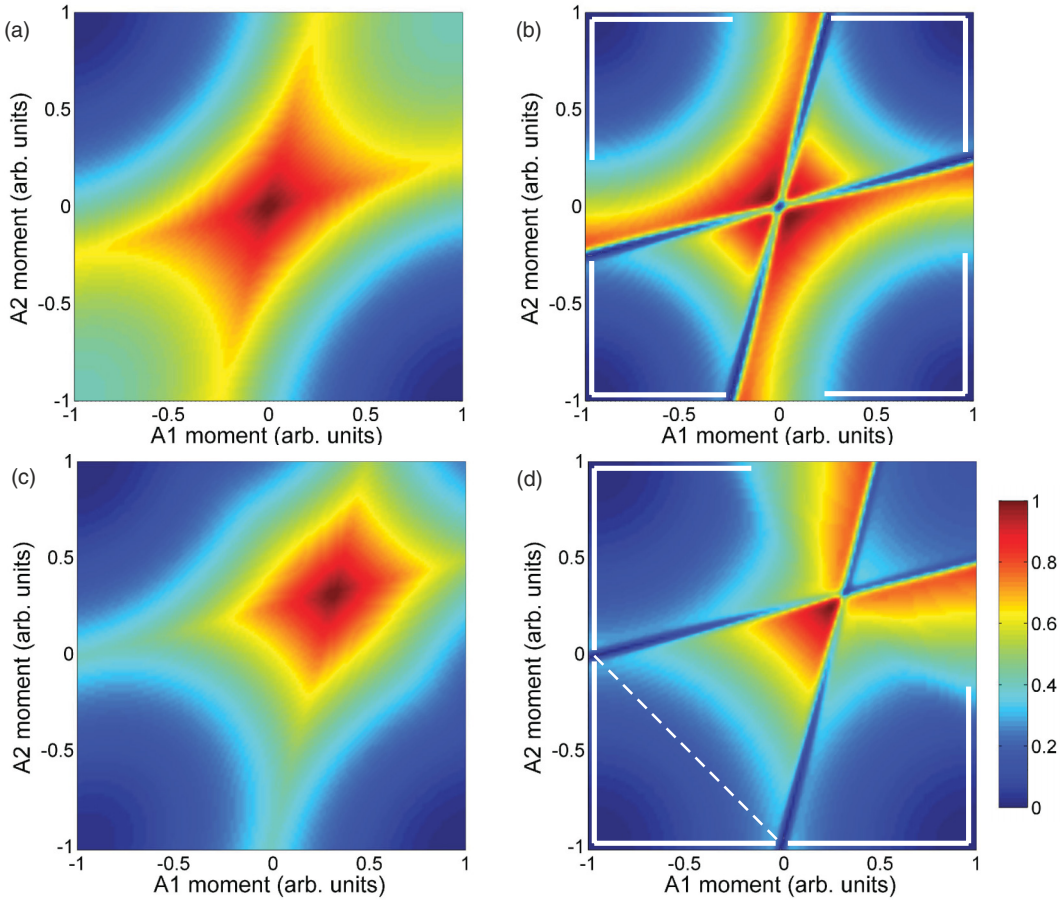


FIG. 3. (Color online) Same as Fig. 2 but at temperature $T = 0.1 \times J_A$.

and it would stay in that configuration, resulting in a ferrimagnetic state with finite total magnetic moment. This finding is in agreement with experimental observations of metamagnetic transitions in the real system, where application of an external field at low temperature ($T < 25$ K) resulted in the generation of a metastable state with finite magnetic moment.[19] It should be noted that if the same calculation were performed while keeping the B-layer moments parallel in the negative direction, the symmetries in Figs. 2(c), 2(d) would be inverted; i.e., the new energy minimum would be at the position $(1,1)$.

When we go to lower temperature ($T = 0.1 \times J_A$), the situation is similar but the borders between possible layer configurations become much sharper (see Fig. 3). The symmetries for both systems remain exactly the same but the sharp borders suggest that the system is locked in a specific configuration. The system with composition $x = 1.0$ [Figs. 3(a), 3(b)] now has no possible switching mechanisms and the layer moments may only exhibit local variations, as seen by the white lines in the landscape.

For the system with $x = 0.8$, however, switching of the layer moments is possible, but the presence of sharp borders suggests that the system needs to jump from one configuration to another. This is made clear when comparing panels (c) and (d) of Fig. 3: The equation of state shows a sharp minimum border, which begins at $(-1,0)$ and $(0,-1)$. At the same locations the energy landscape exhibits local maxima. This means that although the system is allowed to assume that configuration, it will need to overcome the energy barrier (during a switching process). This will, in turn, manifest a metamagnetic transition, where the system jumps between layer configurations. This is also in agreement with experimental observations of strong magnetization jumps in the hemo-ilmenite system with $x = 0.8$ and 0.9 at low temperature ($T < 3$ K), which were investigated by means of Monte Carlo simulations, and revealed collective layer-moment switching.[27]

We now turn our focus on the behavior of the B layers in the system with $x = 0.8$. Since the A layers are the major moment carriers, they will impact the total energy of the system, and thus the dynamics of the B layers. We therefore consider the two scenarios where (i) A layers are fixed at a parallel configuration $(1,1)$, and (ii) the A layers are fixed in an antiparallel configuration $(1,-1)$. Then we calculate the energy landscape and the equation of state as a function of the B-layer moments. The results are seen in Fig. 4. The top panels in the figure show calculations with scenario (i), where the A layers are parallel. As can be clearly seen from the energy and the state of the system, the B layers prefer a quasiparallel alignment in the negative direction, i.e., in the direction opposing that of the parallel A layers. The energy landscape has one global minimum at $(m_{B1},m_{B2}) = (-0.5,-1)$ and the equation of state is minimum at $(-1,-1)$. Considering that

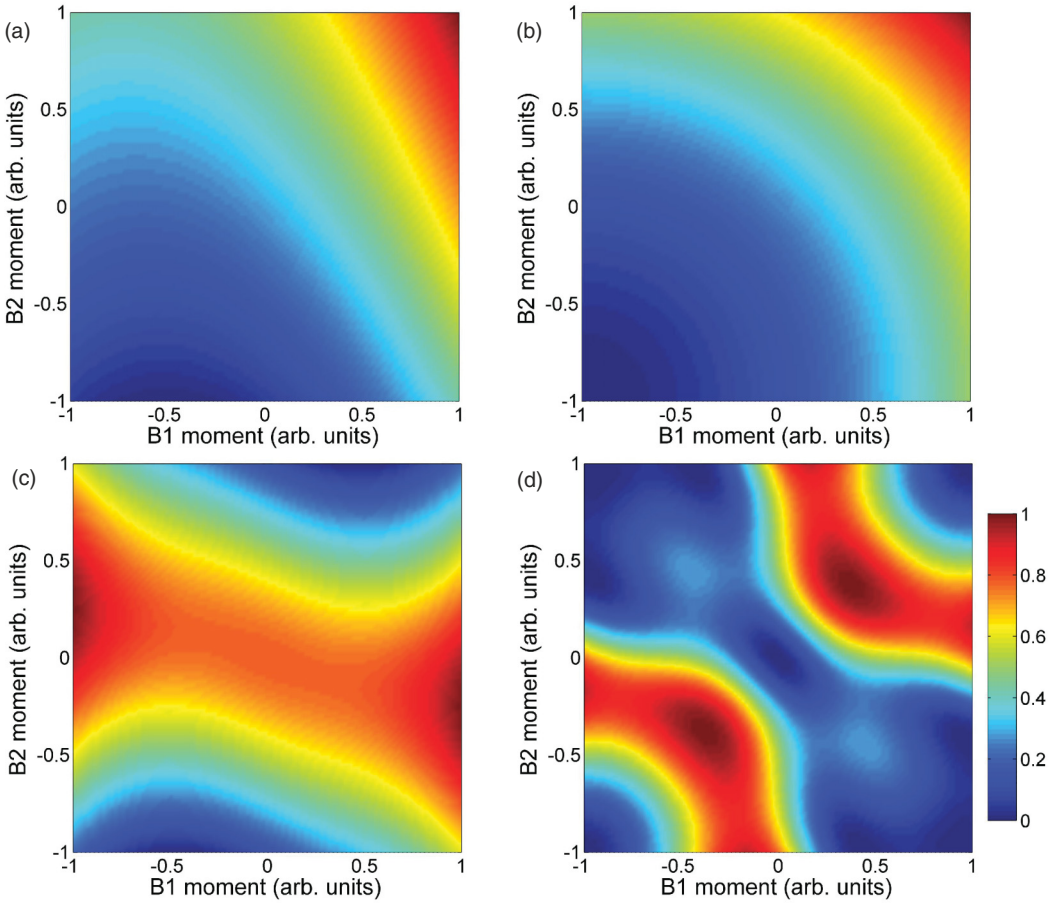


FIG. 4. (Color online) Energy landscape (left) and equation of state (right) calculated using Eqs. (4) and (6), respectively, for compositions $x = 0.8$ as a function of B-layer moments at $T = 0.1 \times J_A$. (a) and (b) show the case when the A-layer moments are (1,1), and (c) and (d) show the case when the A-layer moments are (1,−1). The color bar on the right indicates the value of the normalized landscapes.

the state of the system needs to be satisfied, the negative configuration with (−1,−1) will be the preferred state. This result reflects the previous finding that A-layer moments are generally antiparallel to B-layer moments. This is mediated via the $J_{AB}$ exchange, which is negative.

If we calculate the energy and state of the system using scenario (ii), i.e., an antiparallel A-layer configuration, the situation changes strongly. As seen in Figs. 4(c), 4(d), the B-layer moments have two possible configurations: (1) $(m_{B1},m_{B2}) = (-0.5,-1)$, which has a negative net moment, and (2) $(m_{B1},m_{B2}) = (0.5,1)$, which has a positive net moment. The two possible states have the same probability, as can be seen by the equally low energy levels at those configurations.

From this finding we may conclude that when the A-layer moments transfer from parallel to antiparallel, and thus cancel each other out, the net moment of the system will be that of the B layers. As seen by these calculations, the net moment can be either negative or positive with respect to the original direction of the parallel A-layer moments. Considering that the B-layer moments were in the negative regime in the original scenario, they will remain in the negative configuration. Therefore, by this mechanism the system may exhibit a self-reversal of the net magnetic moment when the A-layers change from parallel to antiparallel. This canceling out of the A-layer moments may occur, e.g., during heating of the system, when the energy barrier between parallel and antiparallel configuration becomes very low (compare Fig. 2).

Finally, we can deduce the possible ordering schemes of the system with $x = 0.8$ using the energy and system state. If we cool the system from $T > T_C$, the A layers assume an antiparallel configuration so that the system dwells in one of the two global minima [Fig. 2(c)]. This means that the B layers have two possible configurations which would result either in a net positive moment or a net negative moment. Therefore, the total moment of the system would be the net moment of the B layers, considering that the A layers cancel each other out. If, however, we apply an external field at low temperature and force the A layers in a parallel alignment, they will dwell in the local minimum [see Fig. 2(d)] and the system will have a large positive net magnetic moment. The B layers will have to assume a negative configuration so that the system transfers to the global minimum of Figs. 4(a), 4(b). When the A layers return to an antiparallel configuration the net moment of the system is again that of the B layers and it will have a negative direction, as discussed above. With this in mind, we can compare these theoretical findings to experimental observations in the $FeTiO_3$-$Fe_2O_3$ system with high Ti content. The metamagnetic transitions observed at low

temperature ($T < 3.0$ K) for compounds with composition $x = 0.9$ and 0.8[27] correspond to reconfiguration of the Fe-rich layers in the model upon crossing the sharp energy barriers in Fig. 3. Moreover, the magnetization self-reversal observed after field cooling in the real systems[28] corresponds to scenario (i) mentioned above, where field cooling forces A layers in a parallel configuration and upon heating the layers become antiparallel, leaving the compound with the negative net moment of the B layers.

## IV. CONCLUSIONS

In conclusion, we have demonstrated that the frustration in this partitioned structure becomes organized, provided that the partitions (layers) act collectively, and that the presence of both Fe(II) and Fe(III) creates additional minima in the energy landscape. Under such conditions it is possible to shift the physical location of frustration and thus control the macroscopic behavior of the system by the application of an external force. Our findings extend beyond magnetism, with implications for a variety of strongly correlated systems with coupled degrees of freedom, illustrating how changes in the energy balance between interacting agents can influence macroscopic phenomena. The presented principle of organized frustration and energy balance is vital and may also be relevant in other scientific fields, where interacting units with conflicting demands attempt to reach an optimized state in a frame of consensual compromise.

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