Geometric frustration in the mixed layer pnictide oxides

M. Enjalran, R.T. Scalettar, and S.M. Kauzlarich

Abstract: We present results from a Monte Carlo investigation of a simple bilayer model with geometrically frustrated interactions similar to those found in the mixed layer pnictide oxides ($Sr_2Mn_3Pn_2O_2$, Pn = As, Sb). Our model is composed of two inequivalent square lattices with nearest-neighbor intralayer and interlayer interactions. We find a ground state composed of two independent Néel-ordered layers when the interlayer exchange is an order of magnitude weaker than the intralayer exchange, as suggested by experiment. We observe this result independent of the number of layers in our model. We find evidence for local orthogonal order between the layers, but it occurs in regions of parameter space that are not experimentally realized. We conclude that frustration caused by nearest-neighbor interactions in the mixed layer pnictide oxides is not sufficient to explain the long-range orthogonal order that is observed experimentally, and that it is likely that other terms (e.g., local anisotropies) in the Hamiltonian are required to explain the magnetic behavior.

PACS Nos.: 75.10Hk, 75.40Mg, 75.50-y, 75.25+z

Résumé : Nous présentons les résultats d'une étude Monte Carlo d'un modèle simple bi-couche avec interaction géométriquement frustrée similaire à celle trouvée dans les oxides pnictides ($Sr_2Mn_3Pn_2O_2$, Pn = As, Sb). Notre modèle est composé de deux réseaux carrés inéquivalents avec interactions plus proche voisin intra-couche et entre les couches. Nous trouvons un fondamental composé de deux couches indépendantes ordonnées de type de Néel lorsque l'interaction entre les couches est un ordre de grandeur plus faible que l'interaction intra-couche, tel que suggéré par l'expérience. Ce résultat reste valable indépendamment du nombre de couches dans notre modèle. Il peut exister un ordre orthogonal entre les couches, mais ceci ne se produit que dans des régions de l'espace des paramètres qui ne sont pas expérimentalement réalisables. Nous en concluons que la frustration causée par l'interaction plus proche voisin dans ce type d'oxide à couches mixes n'est pas suffisante pour expliquer l'ordonnance orthogonale à longue portée observée et qu'il est probable que d'autres termes (par exemple d'anisotropie locale) doivent apparaître dans le Hamiltonien pour expliquer le comportement magnétique.

[Traduit par la Rédaction]

Received June 6, 2000. Accepted August 8, 2001. Published on the NRC Research Press Web site on November 2, 2001.

M. Enjalran.[1] Department of Physics, University of California, Davis, CA 95616, U.S.A. and Materials Research Institute, Lawrence Livermore National Laboratory, University of California, Livermore, CA 94550, U.S.A.
R.T. Scalettar. Department of Physics, University of California, Davis, CA 95616, U.S.A.
S.M. Kauzlarich. Department of Chemistry, University of California, Davis, CA 95616, U.S.A.

[1] Corresponding author : Department of Physics, University of Waterloo, 200 University Avenue, Waterloo, ON N2L 3G1, Canada.

 DOI: 10.1139/cjp-79-11/12-1333

1. Introduction

Clean systems of interacting moments have been studied extensively by analytic and numerical techniques. Although simplified models like Ising, Heisenberg, and Hubbard retain only the most fundamental interactions observed in real materials, they remain tractable to current theoretical techniques, and the study of their ordered phases in various regions of parameter space has contributed enormously to our understanding of magnetic phenomena and the physics of correlated systems [1]. However, real materials are never clean. There is often frustration due to competing interactions and disorder in the interaction strengths.

Competing interactions that cause magnetic frustration can have many origins, lattice geometry, magnetic, and nonmagnetic impurities. In three dimensions, helical magnetic order has been observed when geometric frustration is accompanied by anisotropy [2, 3]. Spin-glass phases are observed when frustration is accompanied by random disorder [4–6]. It has also been suggested that some non-collinear spin-ordered structures belong to a new chiral universality class [7]. The systems we study are essentially two dimensional and contain no anisotropic terms or disorder. Frustration is caused by the lattice geometry. Our primary focus is the orthogonal magnetic structure observed in the mixed layer pnictide oxides [8].

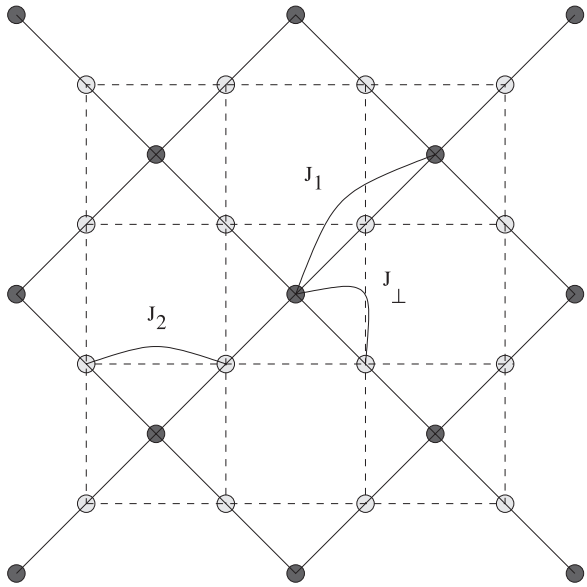
The pnictide oxides of type $A_2Mn_3Pn_2O_2$ (A = Ba, Sr; Pn = As, Sb) are layered anti-ferromagnets that contain two distinct square planes of manganese atoms arranged in a lattice of space group symmetry $I4/mmm$. In one layer, manganese is bonded to oxygen in a planar CuO_2 arrangement, MnO_2^{2-}. In a second layer, it is bonded to a pnictogen in a tetrahedral structure, $MnPn_2^{2-}$, where pnictogen atoms project alternately above and below the plane defined by the manganese atoms. From here on, we denote the two layers as Mn(1) for MnO_2^{2-} and Mn(2) for $MnPn_2^{2-}$. The Mn atoms from the two planes are arranged so that a site in the Mn(1) layer sits directly above and below the center of a square plaquette of Mn atoms in the Mn(2) layer. The manganese carry a spin $S = 5/2$. Frustration can enter through nearest-neighbor interlayer coupling. A more detailed investigation of these systems has been reported elsewhere [9].

2. Model

In all the pnictide oxides except $Sr_2Mn_3As_2O_2$ there is long-range order in the planes that eventually gives rise to weak 3D order. In the compound $Sr_2Mn_3As_2O_2$, there is only short-range order in the Mn(1) planes. The ability of ordered planes to drive c-axis order has been investigated before in the case of layered anti-ferromagnets [10–12]. In $Sr_2Mn_3Sb_2O_2$, magnetic order in the Mn(1) layers is established along the a-axis of the magnetic unit cell, while in the Mn(2) layers the magnetization is along the c-axis. Hence, there is an orthogonal alignment between neighboring layers. Such an ordered state is not without precedent [13, 14]. However, the different temperatures at which the layers order ($T_{\mathrm{Mn(2)}} \approx 300$ K and $T_{\mathrm{Mn(1)}} \approx 65$ K) and the symmetry of the frustrated interlayer interactions, which leads to cancellation, suggest a system of two independent Néel-ordered layers. Previous work has shown that this is not always the case, as thermal or quantum fluctuations (in frustrated systems) can lift the degeneracy of the system to select a single state [15, 16].

To study the effect of frustration on the ground-state magnetic order of the pnictide oxides, we developed a simple model of classical Heisenberg spins with nearest-neighbor intralayer and interlayer interactions. The basic structural unit is a set of two layers, one each of type Mn(1) and Mn(2) (see Fig. 1). The Mn(2) layer has a lattice constant $a = 1$ and contains n^2 sites. The Mn(1) layer is larger by a factor $\sqrt{2}$ and is rotated by $\pi/4$ with respect to the lattice directions of the other layer. The Mn(1) layer contains $n^2/2 + n + 1$ spins. Note that the interlayer coordination is not the same for spins on the two layers. A spin on the Mn(1) plane is coupled to four spins on the Mn(2) plane, and each spin in the Mn(2) plane is coupled to only two spins on the Mn(1) plane.

Fig. 1. A two-dimensional projection of the two distinct layers of the pnictide oxide $Sr_2Mn_3Sb_2O_2$. Sites in the Mn(1) layer are represented by dark circles while sites in the Mn(2) layer are represented by light circles. The intralayer couplings are shown as J_1 and J_2, and the interlayer interaction is indicated by $J_\perp$.



The Hamiltonian for our bilayer model is written as

$$H = J_1 \sum_{i,\boldsymbol{\delta}_1} \vec{S}_i^{(1)} \cdot \vec{S}_{i+\boldsymbol{\delta}_1}^{(1)} + J_2 \sum_{i,\boldsymbol{\delta}_2} \vec{S}_i^{(2)} \cdot \vec{S}_{i+\boldsymbol{\delta}_2}^{(2)} + J_\perp \sum_{i,\boldsymbol{\delta}_\perp} \vec{S}_i^{(\alpha)} \cdot \vec{S}_{i+\boldsymbol{\delta}_\perp}^{(\beta)} \tag{1}$$

The constants J_1, J_2, and $J_\perp$ represent the Mn(1) and Mn(2) intralayer couplings and the interlayer coupling, respectively. The summations of $\boldsymbol{\delta}_\mu$ are over nearest neighbors to site i. For classical spins, one has $|\vec{S}| = (S_x^2 + S_y^2 + S_z^2)^{1/2} = 1$. The relatively large spin-5/2 of the Mn atoms in the pnictide oxides makes this a reasonable approximation.

We studied the equilibrium physics of our model by a single spin-flip Monte Carlo algorithm. We have addressed concerns about proper sampling of phase space by performing simulations with random and ordered initial configurations. We have also considered the effects of the boundary on our finite simulations by employing a few different boundary conditions: open, periodic, and periodic with an effective field on the Mn(1) edge sites. In all cases considered, we found no qualitative difference in our results due to the initial configuration or the conditions imposed at the boundary.

To determine the relative orientation between neighboring spins, either within the same layer or in different layers, we measured a collinear

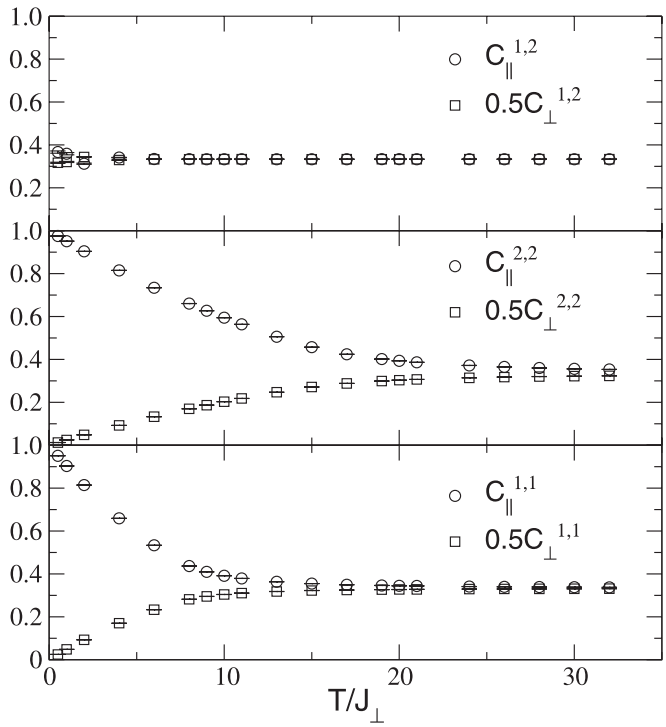
$$C_\parallel^{\alpha,\beta} = \left\langle \frac{1}{zN_\alpha} \sum_i \sum_{\boldsymbol{\delta}} (\vec{S}_i^{\alpha} \cdot \vec{S}_{i+\boldsymbol{\delta}}^{\beta})^2 \right\rangle \tag{2}$$

and a perpendicular

$$C_\perp^{\alpha,\beta} = \left\langle \frac{1}{zN_\alpha} \sum_i \sum_{\boldsymbol{\delta}} (\vec{S}_i^{\alpha} \times \vec{S}_{i+\boldsymbol{\delta}}^{\beta})^2 \right\rangle \tag{3}$$

spin–spin correlation function. Here summations are performed over all nearest neighbors $\boldsymbol{\delta}$ of site i and then over all sites in the lattice; z is the coordination number and N_α is the number of sites in layer α.

Fig. 2. Temperature dependence of the local intra- and interlayer spin–spin correlations in the four layer model with periodic boundary conditions and $J_1 = 1.0$, $J_2 = 2.0$, and $J_\perp = 0.1$. A parallel alignment is favored for intralayer spins when the temperature drops below the respective intralayer coupling; however, the interlayer correlations remain at the high-temperature limit of $1/3$ even for $T \lesssim J_\perp$.



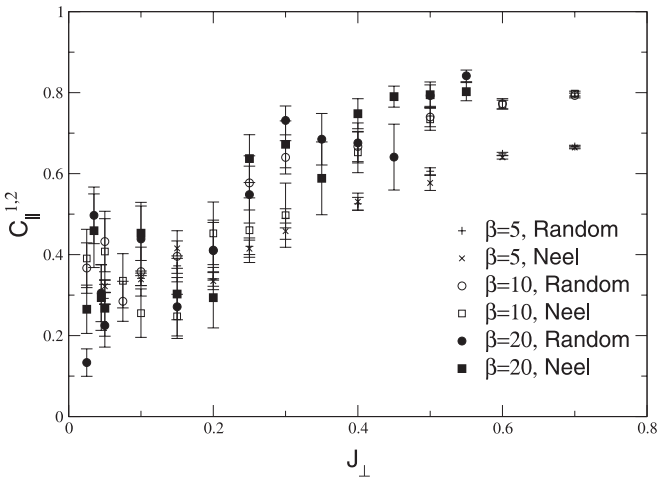
Intralayer correlations are denoted by $\alpha = \beta$ and interlayer correlations are represented by $\alpha \neq \beta$. We stress that $C_\parallel$ and $C_\perp$ measure local correlations. For classical Heisenberg spins, these correlations take on the simple forms $C_\parallel = \langle \cos^2 \theta \rangle$ and $C_\perp = \langle \sin^2 \theta \rangle$. In the high-temperature, paramagnetic, limit, the values $C_\parallel = 1/3$ and $C_\perp = 2/3$ are obtained. We also measured the magnetization and staggered magnetization of each layer.

3. Results and discussion

From the experimental data, representative couplings would set the Mn(2) intralayer exchange to be stronger than the Mn(1) intralayer exchange, with the interlayer interaction weaker by at least an order of magnitude. Therefore, experimentally motivated couplings in our model were set to $J_2 = 2.0$, $J_1 = 1.0$, and $J_\perp = 0.1$. For the results presented herein, systems with 1600 spins per Mn(1) layer and 841 spins per Mn(1) were equilibrated for 15 000 to 25 000 sweeps followed by 15 000 measurement sweeps with 10–25 sweeps between measurements. One Monte Carlo sweep denotes an update of all spins on the lattice.

Our results for a bilayer model indicate that, as a function of temperature, the moments within each layer began to order when the temperature dropped below the respective energy scale, e.g., $T = J_1$ for Mn(1) moments and $T = J_2$ for Mn(2) moments. However, the eventual ground state was a system of two Néel-ordered layers with an arbitrary orientation between the magnetization directions. In a simulation with four layers (i.e., a layered sequence Mn(1)–Mn(2)–Mn(1)–Mn(2)) and periodic boundary conditions along the c-axis, we observed the same qualitative behavior as a function of temperature (see Fig. 2). We emphasize that the interlayer spin–spin correlation function, $C_\parallel^{1,2}$, remained

Fig. 3. Interlayer spin–spin correlations as a function of $J_\perp$ with $J_1 = 1.0$ and $J_2 = 2.0$. The results are for a bilayer model with the initial configuration of the layers being either random or Néel ordered.



at the paramagnetic limit down to low temperatures, $T \lesssim J_\perp$.

We also studied the effect of the strength of frustration on the magnetic ground state. To do this, we fixed the temperature and swept in values of $J_\perp$. For a bilayer model with $J_\perp < 0.25$, we observed two Néel-ordered layers with a paramagnetic interlayer orientation, i.e., $C_\parallel^{1,2} \approx 1/3$ or independent layers. As $J_\perp$ was increased, the two Néel-ordered layers moved towards a collinear state. We observed this behavior independent of the initial configuration (see Fig. 3).

An explanation of these results can be understood by considering the physics of two simpler models, a zigzag lattice and a diagonal lattice, (refer to ref. 9). In the zigzag lattice the frustration is along one crystalline direction; this geometry is similar to the Mn(2) to Mn(1) interlayer interaction. In the limit of weak $J_\perp$, a uniformly canted state is established in the zigzag lattice with orthogonal order obtained in the limit $J_\perp \to 0$. In the diagonal lattice, one has the equivalent of the $J_1 - J_2$ model. This interlayer geometry is analogous to the coupling of Mn(1) sites to Mn(2) sites. In the limit of weak $J_\perp$, the diagonal lattice is composed of two Néel-ordered layers with a collinear alignment. Hence, at weak frustration, it is the competition between these two tendencies in the experimental model that leads to a paramagnetic orientation with large fluctuations. In the case of strong frustration, $J_\perp > 0.5$, the zigzag and diagonal geometries both select a collinear interlayer arrangement.

An orthogonal state for our bilayer model can be found but this phase occurs at couplings strengths that are not supported by experiments (refer to ref. 9). In the case where $J_2 = 0$, the resultant model is a network of intersecting zigzag chains. By setting $J_\perp = 1$ and sweeping in J_1 a transition to a uniformly canted state was observed in the limit of large J_1. For a model with $J_2 = J_\perp = 1.0$, we observed a Néel-ordered Mn(2) layer and a paramagnetic Mn(1) layer, but with Mn(1) spins orthogonal to the local Mn(2) environment, for $J_1 \leq 0.25$. At $J_1 > 0.25$ the system tended toward a state with collinear alignment.

We conclude that frustration caused by nearest-neighbor interactions, both intralayer and interlayer, in the mixed layer pnictide oxides is not sufficient to explain the long-range orthogonal order that is observed experimentally. However, recent work on mixed metal pnictide oxides does indicate that the two distinct layers do not behave independently [17]. In these systems, it is likely that other terms in the Hamiltonian, e.g.,single-ion anisotropies arising from spin-orbit effects, are required to explain the magnetic behavior.

Acknowledgements

We acknowledge the generous support of Campus–Laboratory Collaboration of the University of California, the Materials Research Institute at Lawrence Livermore National Laboratory. We thank Rajiv Singh and Tadashi Ozawa at the University of California, Davis for many useful discussions. We also thank D.P. Landau at the Center for Simulational Physics at the University of Georgia, Athens for helpful suggestions. Work at Lawrence Livermore National Laboratory was performed under the auspices of the U.S. Department of Energy under contract number W-7405-ENG-48.

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