Anisotropic magnetic nearest-neighbor exchange interaction in the pyrite structure: MnTe$_2$, MnS$_2$, and MnSe$_2$

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We consider general anisotropic nearest-neighbor magnetic exchange in the pyrite structure where the magnetic ions occupy the fcc sites. We show how the Dzyaloshinsky-Moriya interaction can stabilize the anticollinear spin configuration observed in MnTe$_2$ when T is slightly below T_N. As an alternative explanation, we also consider the most general symmetric anisotropic nearest-neighbor coupling allowed in the pyrite structure. For MnS$_2$, we construct a model which is consistent with the observed centering, slightly above T_N, of the diffuse neutron scattering around an incommensurate position. We also discuss the spin arrangement observed in MnSe$_2$ when only bilinear spin-spin exchange is present.

I. INTRODUCTION

There have been several experimental studies[1–8] of the properties of the magnetic semiconductors MnTe$_2$, MnS$_2$, and MnSe$_2$. An antiferromagnetic order was found in these pyrite compounds in early neutron-diffraction measurements by Hastings *et al.*[1] The structure develops from the type-III ordering of the fcc system in MnS$_2$ to a type-I structure in MnTe$_2$ through an intermediate-type order in MnSe$_2$. The nature of the phase transitions, as well as the spin structures, has been investigated in detail by neutron-diffraction[1,4–8] and Mössbauer[2] measurements. These experiments have revealed several unusual features in the magnetic behavior.

To explain these features, which are described below, we were led to consider how the geometry of the pyrite structure, illustrated in Fig. 1, affects the spin-spin in-
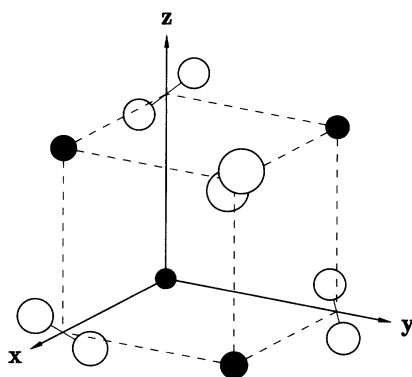

FIG. 1. The pyrite structure. Solid circles denote Mn^{++} cations which form an fcc lattice. Open circles correspond to anion pairs whose axis is along one of the four body diagonals; the groups along the same diagonal are located in a simple cubic lattice. Note the threefold axis (1,1,1) of rotation symmetry about the manganese ion at the origin; every manganese site has a threefold axis along one of the body diagonals.

teractions. We have studied in detail the general form of the anisotropic nearest-neighbor spin-spin exchange. Although it was pointed out[9] long ago that anisotropic interactions, such as the Dzyaloshinsky–Moriya (DM) exchange,[10,11] can be present in the pyrite structure, the forces have not been analyzed any further. More complicated four-spin exchange interactions have been invoked in order to understand the observed features.[12,13] Our work shows, however, that physically more appealing anisotropic nearest-neighbor interactions can explain several unusual properties of manganese pyrites.

Recent neutron-diffraction measurements have established that the type-III structure in MnS$_2$ is collinear[7] whereas Mössbauer experiments[2] have shown that the type-I configuration of MnTe$_2$ is anticollinear. While the stability of the collinear structure in MnS$_2$ can be attributed to thermal and quantum-mechanical fluctuations,[14] it is unknown why the same mechanism is not operational in MnTe$_2$. We find that this can be understood by considering anisotropic exchange: The spin structure is more easily affected by anisotropic interaction in type-I configurations since the magnetic and the chemical unit cells are identical, unlike in type-III configurations.

Chattopadhyay *et al.*[8] have observed that the diffuse neutron scattering in MnS$_2$ is centered at an incommensurate position $\mathbf{q} \approx (\pi/a)(1, 0.44, 0)$ above the Néel temperature T_N although type-III ordering with $\mathbf{Q} = (\pi/a)(1, \frac{1}{2}, 0)$ is found below T_N. These experimentalists suggested that this could result from anisotropic exchange interactions in analogy with the behavior of UAs, as observed and analyzed by Sinha *et al.*[15] To demonstrate that this can, indeed, be the case, we consider a model for which, owing to a DM interaction, the mean-field approach suggests incommensurate $\mathbf{Q} \approx (\pi/a)(1, 0.44, 0)$ order. It is crucial to introduce the low pyrite symmetry to the model since it is impossible to obtain an analogous result, including anisotropy, only in terms of the general nearest-neighbor and next-nearest-neighbor interactions with the fcc symmetry. Apart from

this important difference it is plausible that the behavior of MnS_2 can be understood with the scenario of Sinha *et al.*

While the structures in MnS_2 and $MnTe_2$ are of well-known principal types[11] of magnetic order in an fcc lattice, the structure of $MnSe_2$ is unconventional[1] and cannot be stabilized by the use of an isotropic nearest- and next-nearest-neighbor exchange interactions. We consider the possibility to stabilize this kind of structure by the use of anisotropic nearest-neighbor interaction, but find it difficult to obtain agreement with all observed features of the magnetic structure. We give a summary of various possible explanations.

Our interest in this subject was drawn by some similarities between the observed magnetically ordered structures of $MnSe_2$ and of nuclear spins in copper at nanokelvin temperatures.[16] In small external fields, the copper nuclei also simultaneously display antiferromagnetic Bragg reflections at two positions in **k** space, corresponding to the type-I and the $\mathbf{k} = \mathbf{G}/3$ ordering vectors with[17] $\mathbf{G} = (\pi/a)(2,2,0)$. Anisotropy of spin-spin interactions is crucial in determining the spin configurations of copper as well.[18]

The organization of our paper is as follows. The general form of the nearest-neighbor interaction in the pyrite structure is described in Sec. II. The results are applied to $MnTe_2$, MnS_2, and $MnSe_2$ in Sec. III. Section IV summarizes our work. Finally, the details of the computational method used in the mean-field calculations, as well as considerations on the magnetic structure of $MnSe_2$, are presented in two appendixes.

II. ANISOTROPY
IN THE PYRITE STRUCTURE

For the Hamiltonian we assume

$$\mathcal{H} = \tfrac{1}{2} \sum_{i,j} \mathbf{S}_i \cdot \underline{A}_{ij} \cdot \mathbf{S}_j , \qquad (1)$$

where, by definition, $\mathbf{S}_i \cdot \underline{A}_{ij} \cdot \mathbf{S}_j = \mathbf{S}_j \cdot \underline{A}_{ji} \cdot \mathbf{S}_i$. We also have $\mathbf{S}_i \cdot \underline{A}_{ij} \cdot \mathbf{S}_j = \mathbf{S}_j \cdot \underline{A}_{ij}^T \cdot \mathbf{S}_i$, where $\underline{A}_{ij}^T$ is the transpose of $\underline{A}_{ij}$. Thus $\underline{A}_{ij}^T = \underline{A}_{ji}$. The spin-spin interaction matrix $\underline{A}_{ij}$ can, in particular, contain an antisymmetric part, i.e., the Dzyaloshinsky-Moriya (DM) exchange.[11] We also discuss the general anisotropic symmetric interaction.

Consider the bond ij between nearest-neighbor Mn^{++} ions. We can write the positions $\mathbf{X}^{(k)}$ of the Te, S, or Se anions as

$$\mathbf{X}^{(k)} = (\mathbf{r}_i + \mathbf{r}_j)/2 + \mathbf{X}_{ij}^{(k)} . \qquad (2)$$

For two nearest-neighbor bonds, ij and qr, the sets $\{\mathbf{X}_{ij}^{(k)}\}$ and $\{\mathbf{X}_{qr}^{(k)}\}$ of all positions of the X ions are related by an orthogonal matrix $\underline{R}$: $\{\mathbf{X}_{qr}^{(k)}\} = \{\underline{R}\mathbf{X}_{ij}^{(k)}\}$; in particular, $\hat{\mathbf{r}}_{qr} = \underline{R}\hat{\mathbf{r}}_{ij}$ or $\hat{\mathbf{r}}_{qr} = \underline{R}\hat{\mathbf{r}}_{ji}$ where $\hat{\mathbf{r}}_{ij} = (\mathbf{r}_j - \mathbf{r}_i)/|\mathbf{r}_j - \mathbf{r}_i|$. Note that $\underline{R}$ may contain an inversion. One can now write the transformation rule for the matrix $\underline{A}_{ij}$ as

$$\underline{A}_{qr} = \begin{cases} \underline{R}\underline{A}_{ij}\underline{R}^T & \text{for } \hat{\mathbf{r}}_{qr} = \underline{R}\hat{\mathbf{r}}_{ij} , \\ \underline{R}\underline{A}_{ji}\underline{R}^T & \text{for } \hat{\mathbf{r}}_{qr} = \underline{R}\hat{\mathbf{r}}_{ji} . \end{cases} \qquad (3)$$

This equation states the constraints imposed by crystal symmetry on the Hamiltonians which are bilinear in $\mathbf{S}_i$; as such Eq. (3) is the cornerstone of our analysis of Eq. (1). If $\det \underline{R} = 1$ we have pure rotation and Eq. (3) is evidently true; when $\det \underline{R} = -1$ we have assumed that $\underline{A}_{ij}$ can, in principle, be written in terms of polar vectors without the use of quantities, such as $\mathbf{a} \times \mathbf{b} \cdot \mathbf{c}$, which depend on left or right handedness. Usually one can restrict the possible form of $\underline{A}_{ij}$ because all matrices $\underline{R}$ must give identical $\underline{A}_{qr}$. In the pyrite structure, however, there is, owing to the low local symmetry, only one matrix $\underline{R}$ which transforms two given nearest-neighbor spin-spin bonds to each other. Thus $\underline{A}_{ij}$ is of general form. It contains a symmetric and an antisymmetric part with six and three parameters, respectively.

It is useful to define the interaction matrix $\underline{A}_{ij}$ in terms of parameters which are more directly related to the local symmetry than the components of $\underline{A}_{ij}$. In order to accomplish this, we characterize each bond ij by a local orthonormal basis $(\hat{\mathbf{s}}_{ij}, \hat{\mathbf{t}}_{ij}, \hat{\mathbf{u}}_{ij})$ which is selected so that the basis for the bond qr is $(\hat{\mathbf{s}}_{qr}, \hat{\mathbf{t}}_{qr}, \hat{\mathbf{u}}_{qr}) = (\underline{R}\hat{\mathbf{s}}_{ij}, \underline{R}\hat{\mathbf{t}}_{ij}, \underline{R}\hat{\mathbf{u}}_{ij})$. We define the basis $(\hat{\mathbf{s}}_{ij}, \hat{\mathbf{t}}_{ij}, \hat{\mathbf{u}}_{ij})$ relative to the local geometry as shown in Fig. 2. Vectors $(\hat{\mathbf{s}}_{ij}, \hat{\mathbf{t}}_{ij}, \hat{\mathbf{u}}_{ij})$ are defined so that they are eigenvectors of the interaction matrix $\underline{A}_{ij}$ for ideal fcc symmetry, $\hat{\mathbf{u}}_{ij} = \pm\hat{\mathbf{r}}_{ij}$ and, if $\hat{\mathbf{r}}_{ij} = (1/\sqrt{2})(1,1,0)$, we have $\hat{\mathbf{t}}_{ij} = \pm(0,0,1)$ and $\hat{\mathbf{s}}_{ij} = \pm(1/\sqrt{2})(1,-1,0)$; see Fig. 2. However, the geometry of the pyrite structure makes it possible to assign for these vectors a well-defined direction which is determined by the nearby anion pairs.

More explicitly, we list the vectors $\mathbf{X}_{ij}^{(k)}$ of Eq. (2) for the nonmagnetic anions shown in Fig. 2:

$$\begin{aligned} \mathbf{X}_{ij}^{(1)} &= a\hat{\mathbf{s}}_{ij}/\sqrt{2} + b(\hat{\mathbf{t}}_{ij} + \sqrt{2}\hat{\mathbf{u}}_{ij})/(2\sqrt{3}), \\ \mathbf{X}_{ij}^{(2)} &= a\hat{\mathbf{s}}_{ij}/\sqrt{2} - b(\hat{\mathbf{t}}_{ij} + \sqrt{2}\hat{\mathbf{u}}_{ij})/(2\sqrt{3}), \\ \mathbf{X}_{ij}^{(3)} &= -a\hat{\mathbf{s}}_{ij}/\sqrt{2} + b(\hat{\mathbf{t}}_{ij} + \sqrt{2}\hat{\mathbf{s}}_{ij})/(2\sqrt{3}), \\ \mathbf{X}_{ij}^{(4)} &= -a\hat{\mathbf{s}}_{ij}/\sqrt{2} - b(\hat{\mathbf{t}}_{ij} + \sqrt{2}\hat{\mathbf{s}}_{ij})/(2\sqrt{3}). \end{aligned} \qquad (4)$$

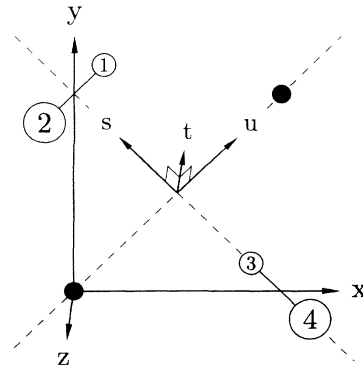Here b is the distance between the nuclei in the anion

FIG. 2. Nearest-neighbor bond in the pyrite structure. Numbers 1–4 refer to Eq. (4). See text for detailed discussion.

pairs, and $a = a_0/2$. These equations are valid for all spin-spin bonds in the pyrite structure. In particular, the signs of vectors $\hat{\mathbf{s}}_{ij}$, $\hat{\mathbf{t}}_{ij}$, and $\hat{\mathbf{u}}_{ij}$ are well defined because the replacements $\hat{\mathbf{s}}_{ij} \rightarrow -\hat{\mathbf{s}}_{ij}$, etc., are not equivalent to permutations of vectors $\mathbf{X}_{ij}^{(k)}$.

A. Dzyaloshinsky-Moriya interaction

We can write the DM interaction $\underline{A}_{ij}^{\mathrm{DM}} = (\underline{A}_{ij} - \underline{A}_{ij}^T)/2$ as

$$\underline{A}_{ij}^{\mathrm{DM}} = (\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_{ij}) \big[D_1(\hat{\mathbf{u}}_{ij}\hat{\mathbf{s}}_{ij} - \hat{\mathbf{s}}_{ij}\hat{\mathbf{u}}_{ij})$$
$$+ D_2(\hat{\mathbf{u}}_{ij}\hat{\mathbf{t}}_{ij} - \hat{\mathbf{t}}_{ij}\hat{\mathbf{u}}_{ij}) + D_3(\hat{\mathbf{s}}_{ij}\hat{\mathbf{t}}_{ij} - \hat{\mathbf{t}}_{ij}\hat{\mathbf{s}}_{ij}) \big] . \quad (5)$$

This is the most general $\underline{A}_{ij}^{\mathrm{DM}}$ for which $(\underline{A}_{ij}^{\mathrm{DM}})^T = \underline{A}_{ji}^{\mathrm{DM}}$ and which is consistent with Eq. (3). The order of subscripts ij is irrelevant for all other vectors on the right-hand side except $\hat{\mathbf{r}}_{ij}$. The DM interaction can also be written as

$$\mathbf{S}_i \cdot \underline{A}_{ij}^{\mathrm{DM}} \cdot \mathbf{S}_j = \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j , \quad (6)$$

where $\mathbf{D}_{ij}$ is a vector coupling constant,

$$\mathbf{D}_{ij} = \hat{\mathbf{r}}_{ij} \times (D_1\hat{\mathbf{s}}_{ij}$$
$$+ D_2\hat{\mathbf{t}}_{ij}) + D_3\big[(\hat{\mathbf{r}}_{ij} \times \hat{\mathbf{s}}_{ij}) \times \hat{\mathbf{u}}_{ij} \big] \times \hat{\mathbf{t}}_{ij} . \quad (7)$$

All terms in this equation have an odd number of cross products; therefore, since $\hat{\mathbf{s}}_{ij}$, $\hat{\mathbf{t}}_{ij}$, $\hat{\mathbf{u}}_{ij}$, and $\hat{\mathbf{r}}_{ij}$ are polar vectors, $\mathbf{D}_{ij}$ is an axial vector. For example, in β-MnS which has zinc-blende structure, we would have[9,11] $\mathbf{D}_{ij} = D\hat{\mathbf{r}}_{ij} \times \hat{\mathbf{d}}_{ij}$, where $\hat{\mathbf{d}}_{ij}$ is determined by the use of a geometric rule[19] in analogy with vectors $\hat{\mathbf{s}}_{ij}$, $\hat{\mathbf{t}}_{ij}$, and $\hat{\mathbf{u}}_{ij}$.

We note that the DM exchange vanishes for next-nearest-neighbor (NNN) pairs ij in the pyrite structure because there is an inversion symmetry about $(\mathbf{r}_i + \mathbf{r}_j)/2$: We can use $\underline{R}' = -\underline{R}$ as well as $\underline{R}$ in Eq. (3) and we find $\underline{A}_{qr} = \underline{A}_{qr}^T$ because $\underline{A}_{ji} = \underline{A}_{ij}^T$.

B. Symmetric anisotropic exchange

The symmetric part $\underline{A}_{ij}^S = (\underline{A}_{ij} + \underline{A}_{ij}^T)/2$ of the nearest-neighbor (NN) interaction $\underline{A}_{ij}$ is

$$\underline{A}_{ij}^S = P_1\hat{\mathbf{s}}_{ij}\hat{\mathbf{s}}_{ij} + P_2\hat{\mathbf{t}}_{ij}\hat{\mathbf{t}}_{ij} + P_3\hat{\mathbf{u}}_{ij}\hat{\mathbf{u}}_{ij}$$
$$+ S_{12}(\hat{\mathbf{s}}_{ij}\hat{\mathbf{t}}_{ij} + \hat{\mathbf{t}}_{ij}\hat{\mathbf{s}}_{ij}) + S_{23}(\hat{\mathbf{t}}_{ij}\hat{\mathbf{u}}_{ij} + \hat{\mathbf{u}}_{ij}\hat{\mathbf{t}}_{ij})$$
$$+ S_{31}(\hat{\mathbf{u}}_{ij}\hat{\mathbf{s}}_{ij} + \hat{\mathbf{s}}_{ij}\hat{\mathbf{u}}_{ij}) . \quad (8)$$

Equation (3) is again guaranteed by the definition of vectors $\hat{\mathbf{s}}_{ij}$, $\hat{\mathbf{t}}_{ij}$, and $\hat{\mathbf{u}}_{ij}$. The isotropic nearest-neighbor coupling constant can be defined as $J_1 = (P_1 + P_2 + P_3)/3$, and deviations of P_1, P_2, and P_3 from J_1 gives the pseudodipolar part of the interaction. In fcc systems, P_1, P_2, and P_3 specify completely the nearest-neighbor coupling. However, the low symmetry of the pyrite structure allows the three other quantities S_{12}, S_{23}, and S_{31}, and the prin-

cipal axes of the interaction matrix can differ from their orientations in fcc systems. For example, $\underline{S}_{12}$ rotates the eigenvectors of $\underline{A}_{ij}^S$ in the plane of $\hat{\mathbf{s}}_{ij}$ and $\hat{\mathbf{t}}_{ij}$.

III. APPLICATIONS

A. MnTe$_2$

In the pyrite structure, Fig. 1, the Mn^{++} cations with magnetic moments are located in an fcc lattice, but the chemical unit cell contains four magnetic ions dividing the system into four simple cubic sublattices. In this case (see Appendix A) it is easy to understand that there can be a direct coupling between Fourier components which differ by the vectors

$$\mathbf{K}_1 = (\pi/a)(1,0,0), \quad \mathbf{K}_2 = (\pi/a)(0,1,0),$$
$$\mathbf{K}_3 = (\pi/a)(0,0,1) , \quad (9)$$

where the fcc lattice constant $a_0 = 2a$. Since type-I configurations contain Fourier components with these wave vectors, it is likely that the structure is of the multi-k type. Indeed, according to Mössbauer experiments,[2] the spin configuration of MnTe$_2$ is

$$\mathbf{S}_i \propto \frac{1}{\sqrt{3}} \left[\hat{\mathbf{y}} \cos(\mathbf{K}_1 \cdot \mathbf{r}_i) + \hat{\mathbf{z}} \cos(\mathbf{K}_2 \cdot \mathbf{r}_i) + \hat{\mathbf{x}} \cos(\mathbf{K}_3 \cdot \mathbf{r}_i) \right]$$
$$(10)$$

at temperatures immediately below T_N; this is the "anti-collinear" type-I configuration. This structure minimizes the dipolar energy for type-I order since the spin components are perpendicular to the corresponding wave vectors, as was found already in the first powder neutron-diffraction experiments.[1] The spins in this structure are parallel to the axes of the threefold rotation symmetry; see Fig. 1.

There are many ways to stabilize the structure defined by Eq. (10) using anisotropic nearest-neighbor coupling. For simplicity we ignore the pseudodipolar part of the NN interaction; i.e., we take $P_1 = P_2 = P_3 = J_1 > 0$. We also include isotropic ferromagnetic NNN coupling: $J_2 < 0$. In this case we find that the configuration specified by Eq. (10) is the classical ground state of the spin system if we assume, for example, a DM exchange with

$$D_1 \geq 0 , \quad D_2 \leq 0 , \quad D_3 \geq 0 . \quad (11)$$

We obtain this result for symmetric anisotropic interaction as well, when (e.g.)

$$S_{12} \leq 0 , \quad S_{23} \leq 0 , \quad S_{31} = 0 \quad (12)$$

and find, therefore, that these two types of anisotropy give rise to qualitatively similar effects.

As an example, we study the model with $J_1 = -20J_2 = 50D_1 > 0$ using the Monte Carlo (MC) simulation; we employ the method of Ref. 20. We define $\mathbf{S}(\mathbf{q}) = N^{-1/2} \sum_i \mathbf{S}(\mathbf{r}_i) \exp(-i\mathbf{q} \cdot \mathbf{r}_i)$ and calculate the MC averages $\langle |\mathbf{S}(\mathbf{K}_m)|^2 \rangle^{1/2}$ decreasing the temperature gradually. 3000 MC updates per spin (MCS) were performed

between changes in temperature; the averages were calculated over the last 2000 MCS. Results for a classical system of $N = 4096$ spins are shown in Fig. 3(a): A triple-$\mathbf{k}$ structure of Eq. (9) emerges below T_N. For reference we present in Fig. 3(b) analogous results for the isotropic model with $J_1 = -20J_2 > 0$ and $D_1 = 0$. In this case the system orders with a collinear single-$\mathbf{k}$ state below T_N.

Comparing the results of Figs. 3(a) and (b) we find that the DM interaction, $D_1 = 0.02J_1$, increases T_N by 10%, i.e., quite substantially. The DM coupling is probably particularly effective in this respect as it completely removes the continuous degeneracies of the model. In fact, it has been argued that the observed critical exponents would be described by using the simple cubic Ising model.[4]

The ratio of the Curie-Weiss constant θ and the Néel temperature T_N can be compared against the measured data. Taking into account the quite large value of $T_N^{\mathrm{MF}}T_N$, which can be inferred from Monte Carlo

simulations,[21,22] one finds that the values of θ/T_N for $MnTe_2$, MnS_2, and $MnSe_2$ can be understood, at least qualitatively, by employing the isotropic model. However, in order to explain the observed spin structures one has to consider other types of spin-spin interactions.

For our model ($D_1 = 0.02J_1$) we have $k_B T_N/J_1 \approx 0.65$ and $k_B\theta = 4J_1 + 2J_2$, and we obtain $\theta/T_N \approx 6.0$; here the effect of D_1 is zero on the asymptotic value of θ. The ratio θ/T_N in this model is close to the experimental value[1,4] $\theta/T_N = 6.1$.

With $D_1 = 0.02J_1$, the effect of temperature is simply to scale the expectation values of $\langle \mathbf{S}_i \rangle$; the spin structure below T_N is always given by Eq. (10), which is in contrast to the experimentally observed deflections from the configuration given by Eq. (10) well below T_N. This effect has been discussed previously introducing a phenomenological model which includes a four-spin interaction and a trigonal anisotropy term.[12] It is, however, well known that there are effects which favor collinear states in Heisenberg models.[14] In our example the DM anisotropy $D_1 = 0.02J_1$ is large enough to overcome thermal fluctuations which stabilize a collinear structure[14] when $D_1 = 0$. Quantum-mechanical effects also tend to stabilize collinear states[23] and might well be large enough to compete with the DM energy, thus providing an alternate explanation to that given in Ref. 12.

B. MnS_2

Recent experiments[8] have shown that diffuse neutron scattering in $MnSe_2$ above T_N is centered around the incommensurate position $\mathbf{q} \approx (\pi/a)(1, 0.44, 0)$, although below T_N a collinear commensurate type-III structure has been observed. As this kind of behavior is unusual, it is tempting to connect the situation with nontrivial properties of the pyrite structure. In order to gain some insight, we study an example of the DM interaction in which the mean-field approach suggest incommensurate ordering with a wave vector $\mathbf{q} \approx (\pi/a)(1, 0.44, 0)$.

Type-III order is stable in the (J_1, J_2) model when $0 < 2J_2 < J_1$. We choose $J_2 = 0.2J_1$ which should be in reasonable agreement with the situation in MnS_2: Apart from its incommensurate centering, the intensity of diffuse neutron scattering above T_N could be fitted well by using[8] $J_2 = 0.23J_1$.

We also include a small nearest-neigbor dipole-dipole interaction by setting $P_1 = P_2 = 1.01J_1$, $P_3 = 0.98J_1$ [Eq. (8)]. For the DM interaction we select $D_1 = 0.07J_1$. The deviation from the fully isotropic model is thus rather small. The lowest eigenvalue $\lambda(\mathbf{q})$ of the interaction matrix $\underline{A}(\mathbf{q})$ (see Appendix A) is shown in Fig. 4(a) as a function of $\mathbf{q} = (\pi/a)(0, x, 0)$; the evolution of the lowest energy eigenvector is illustrated in terms of the corresponding quantities $\mathbf{S}(\mathbf{q} + \mathbf{K}_m)$ [see Eq. (A10)] in Fig. 4(b).

The eigenvector having the lowest eigenvalue $\underline{A}[(\pi/a)(0, x, 0)]$ at $x = 0$ corresponds to the structure given by Eq. (10). The lowest energy eigenvectors for x and $-x$ are degenerate and when $x \to \frac{1}{2}$ one can construct the structure
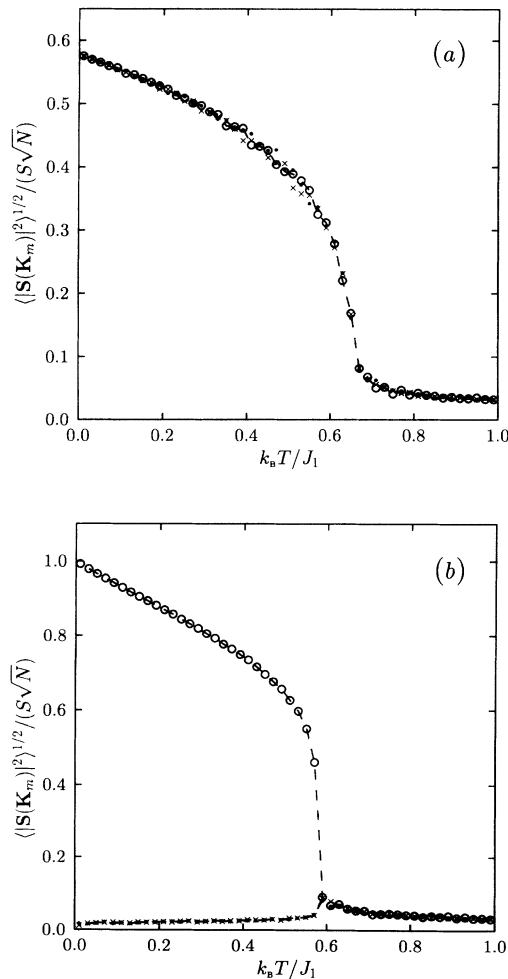
FIG. 3. Monte Carlo averages ($\bigcirc$, $\bullet$, $\times$) of type-I Fourier components $\langle |\mathbf{S}(\mathbf{K}_m)|^2 \rangle^{1/2}$, $m = 1, 2$, and 3, for a model with $J_1 = -20J_2 > 0$ and a DM anisotropy $D_1 = 0.02J_1$ (a), and in the isotropic case $D_1 = 0$ (b). Dashed lines are guides for the eye.

$$\mathbf{S}_i \propto \hat{\mathbf{y}}\sqrt{2}\cos\left[\frac{\pi}{a}\left(1,\frac{1}{2},0\right)\cdot\mathbf{r}_i + \frac{\pi}{4}\right], \qquad (13)$$

i.e., a collinear type-III configuration. Here the dipole-dipole interaction selects the $\frac{1}{2}$ direction of the wave vector as an easy axis along which spins are oriented in collinear structures. The DM energy vanishes in this case, indicating that an interaction with $D_1 > 0$ cannot efficiently produce canted type-III structures. However, a nonzero DM energy results if the wave vector of magnetic order differs from $\mathbf{Q} = (\pi/a)(1,\frac{1}{2},0)$, and therefore, the minimum of $\lambda(\mathbf{q})$ is slightly deflected from this position.

The actual transitions at T_N can still directly take place to the commensurate, collinear type-III configuration, through a fluctuation-driven first-order transition, in a manner similar to that observed[15] in UAs. In the low-T limit, below the critical region around T_N, the stability of the type-III structure vs the incommensu-

rate wave vector corresponding to the minimum of $\lambda(\mathbf{q})$ can probably be understood as a result from the general tendency to form a structure with equal sublattice magnetizations.[24,18] The most common equal-moment structure with an incommensurate wave vector, a helical spin configuration, is not energetically particularly favorable since $\lambda_{min}[\mathbf{q} = (\pi/a)(1,0.44,0)[$ does not have easy-plane anisotropy, as shown by Fig. 4.

C. MnSe$_2$

According to neutron-diffraction measurements,[1] the principal ordering vector of MnSe$_2$ is $\mathbf{Q} = (\pi/a)(1,1/3,0)$; the magnetic unit cell thus triples the chemical unit cell in the direction of the 1/3 component (Appendix B). As Fig. 4(a) shows, it is possible that the minimum eigenvalue is at an incommensurate position $\mathbf{q} = (\pi/a)(1,x,0)$ and, for suitable parameters, it can be arbitrarily close to $x = \frac{1}{3}$. Therefore bilinear exchange alone can stabilize a structure with the $\mathbf{Q} = (\pi/a)(1,\frac{1}{3},0)$ order. For satisfactory agreement with experiments, it would also be necessary to stabilize a structure in which magnetic moments are along the $\frac{1}{3}$ directions of the wave vector, and which exhibits the observed third harmonic fundamental ordering vector (see Appendix B): These features can probably be studied reliably only by the use of Monte Carlo simulations. We were, however, not able to produce the observed structure in detail taking into account only interactions up to next-nearest-neighbor exchange: The various possibilities are summarized in Appendix B.

IV. DISCUSSION AND SUMMARY

We have analyzed the nearest-neighbor magnetic exchange interaction in the pyrite structure MnX_2 where the magnetic Mn^{++} ions occupy the fcc sites. The presence of the four anion pairs with different alignments in the chemical cell brings about important changes in the coupling between the magnetic ions. We explicitly constructed the most general interaction matrices for the symmetric and the antisymmetric anisotropic interactions, the latter being known as the Dzyaloshinsky-Moriya (DM) interaction.

Our general results were applied in an effort to explain some interesting properties of manganese pyrites on the basis of a dominating nearest-neighbor exchange interaction. We demonstrated that the DM interaction can stabilize the anticollinear spin configuration observed in MnTe$_2$ when T is slightly below[2] T_N. This structure can also result from the symmetric part of the anisotropic coupling. For MnS$_2$, we constructed a model which is consistent with the observed centering of diffuse neutron scattering around an incommensurate position $\mathbf{q} \approx (\pi/a)(1,0.44,0)$, at temperatures slightly above[8] T_N. Our model also has the property that the DM energy vanishes at $x = \frac{1}{2}$ so that no sublattice canting is produced for type-III order, consistently with the observed[7] collinearity of the structure. Using a model
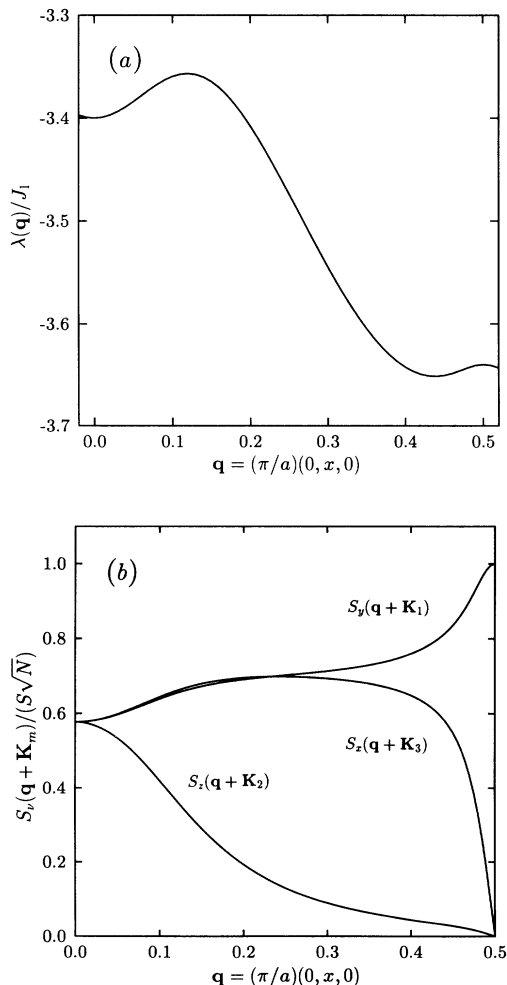

FIG. 4. (a) Smallest eigenvalue of $\underline{A}(\mathbf{q})$ along the line $\mathbf{q} = (\pi/a)(0,x,0)$, $0 < x < \frac{1}{2}$, when $J_1 > 0$, $P_1 = P_2 = 1.01J_1$, $P_3 = 0.98J_1$, $J_2 = 0.2J_1$, and $D_1 = 0.07J_1$. (b) Lowest energy eigenvector as a combination of four fcc Fourier amplitudes; only the nonzero components of $\mathbf{S}(\mathbf{q} + \mathbf{K}_m)$ are shown; $\mathbf{S}(\mathbf{q}) = 0$.

with only bilinear nearest-neighbor interactions, we were unable to obtain the experimentally determined[1,6] spin configuration of $MnSe_2$, although the fundamental ordering vector $\mathbf{Q} = (\pi/a)(1, \frac{1}{3}, 0)$ itself could be stabilized. In principle, the observed spin structure can be understood by introducing an appropriate eighth-nearest-neighbor interaction. Measurement of diffuse neutron scattering in $MnSe_2$ could give valuable more detailed information about interaction parameters. In any case, our results clearly show that anisotropic exchange interactions can be important in the manganese pyrites. We also hope that our work stimulates first principles calculations[25] of such interactions.

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APPENDIX A: MEAN-FIELD THEORY

If the system has n magnetic moments in the the chemical unit cell, it is useful to write the Hamiltonian[11]

$$\mathcal{H} = \frac{1}{2} \sum_{\mu,\nu} \sum_{l,m} \mathbf{S}_{l\mu} \cdot \underline{A}_{l\mu,m\nu} \cdot \mathbf{S}_{m\nu} \ . \qquad (A1)$$

Here subscripts denote the lattice site $\mathbf{r}_{l\mu} = \mathbf{r}_{l0} + \rho_\mu$, where $\rho_0, \ldots, \rho_{n-1}$ runs through all magnetic sites in the zeroth unit cell, and the vector $\mathbf{r}_{l0}$ gives the position of the zeroth site of the lth unit cell; the points $\mathbf{r}_{l0}$ form a Bravais lattice. For pyrites, we have $n = 4$.

We introduce Fourier transformations over $\mathbf{r}_{l0}$:

$$\mathbf{S}_{l\mu} = \sqrt{\frac{n}{N}} \sum_{\mathbf{k}} \mathbf{S}_\mu(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}_{l\mu}), \qquad (A2)$$

$$\underline{A}_{l\mu,m\nu} = \frac{n}{N} \sum_{\mathbf{k}} \underline{A}_{\mu\nu}(\mathbf{k}) \exp\left[i\mathbf{k} \cdot (\mathbf{r}_{l\mu} - \mathbf{r}_{m\nu})\right]. \quad (A3)$$

In terms of these the Hamiltonian assumes the form

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{k}} \sum_{\mu,\nu} \mathbf{S}_\mu^*(\mathbf{k}) \cdot \underline{A}_{\mu\nu}(\mathbf{k}) \cdot \mathbf{S}_\nu(\mathbf{k})$$

$$= \frac{1}{2} \sum_{\mathbf{k}} \mathcal{S}^*(\mathbf{k}) \cdot \underline{A}(\mathbf{k}) \cdot \mathcal{S}(\mathbf{k}) \ , \qquad (A4)$$

where $\mathcal{S}(\mathbf{k}) = (\mathbf{S}_0(\mathbf{k}), \ldots, \mathbf{S}_{n-1}(\mathbf{k}))$ is a vector with $3n$ components, and $\underline{A}(\mathbf{k})$ is a symmetric $3n \times 3n$ matrix. $\underline{A}(\mathbf{k})$ is symmetric even if it contains an antisymmetric DM exchange, because when calculating the transpose of $\underline{A}(\mathbf{k})$ we interchange both indices referring to the Cartesian components of the spins as well as the sublattice indices μ, ν: The minus signs cancel. We write $\underline{A}(\mathbf{k})$ using eigenvalues $\lambda^{(a)}(\mathbf{k})$ and normalized eigenvectors $\mathbf{e}^{(a)}(\mathbf{k})$,

$$\underline{A}(\mathbf{k}) = \sum_{a=1}^{3n} \lambda^{(a)}(\mathbf{k}) \mathbf{e}^{(a)}(\mathbf{k}) \mathbf{e}^{(a)}(\mathbf{k}) \ , \qquad (A5)$$

and obtain finally

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{k}} \sum_{a=1}^{3n} \lambda^{(a)}(\mathbf{k}) |\mathbf{e}^{(a)}(\mathbf{k}) \cdot \mathcal{S}(\mathbf{k})|^2 \ . \qquad (A6)$$

If we can fulfill the conditions $|\mathbf{S}_{l\mu}| = S$, expressing $\mathcal{S}(\mathbf{k})$ using only eigenvectors $\mathbf{e}^{(b)}(\mathbf{q})$ which belong to the lowest eigenvalue $\lambda = \min_{a,\mathbf{k}} \lambda^{(a)}(\mathbf{k})$, we have solved the classical ground state problem. After this we can extend the solution to $T > 0$ employing the formulas

$$\langle \mathbf{S}_{l\mu} \rangle(T) = p(T)\, \mathbf{S}_{l\mu}(T = 0) \ , \qquad (A7)$$

$$p(T) = B_S\left[-S^2 \lambda\, p(T)/T \right] \ , \qquad (A8)$$

where $B_S(x)$ is the Brillouin function.

Let us consider the case when points $\mathbf{r}_{l\mu}$ constitute a Bravais lattice but nonmagnetic ions reduce the local symmetry so that exchange interactions are different for various sites in the chemical unit cell. For simplicity we assume that $|\mathbf{S}_{l\mu}| = S$, using only one eigenvector $\mathbf{e}^{(a)}(\mathbf{k}) = (\mathbf{e}_0^{(a)}(\mathbf{k}), \ldots, \mathbf{e}_{n-1}^{(a)}(\mathbf{k}))$. In this case we have

$$\mathbf{S}_{l\mu} = \sqrt{n} S \mathbf{e}_\mu^{(a)}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}_{l\mu}) \ . \qquad (A9)$$

Working in the original Bravais lattice $\mathbf{r}_{l\mu}$, we then calculate the Fourier transform $\mathbf{S}(\mathbf{q}) = N^{-1/2} \sum_{l\mu} \mathbf{S}_{l\mu} \exp(-i\mathbf{q} \cdot \mathbf{r}_{l\mu})$. The nonzero components are given by

$$\mathbf{S}(\mathbf{k} + \mathbf{K}) = S\sqrt{\frac{N}{n}} \sum_\mu \mathbf{e}_\mu^{(a)}(\mathbf{k}) \exp(-i\mathbf{K} \cdot \rho_\mu) \ , \quad (A10)$$

where $\mathbf{K}$ belongs to the reciprocal lattice of points $\mathbf{r}_{l0}$, but not to the lattice of the $\mathbf{r}_{l\mu}$'s except when $\mathbf{K} = 0$. We see that the ions reducing the local symmetry can give rise to a coupling between Fourier components $\mathbf{S}(\mathbf{Q})$ and $\mathbf{S}(\mathbf{Q} + \mathbf{K})$ in the mean-field theory. For example, weak ferromagnetism[26] can exist if $\mathbf{Q} = \mathbf{K}$, and a structure obtained by superposing members of the star of the ordering vector $\mathbf{Q}_a$ can be stable if the vectors of the star differ by $\mathbf{K}$.

APPENDIX B:
MAGNETIC STRUCTURE OF MnSe$_2$

According to powder neutron diffraction measurements of Ref. 1 the observed Bragg reflections agree well with values calculated assuming

$$\mathbf{S}_i \propto \hat{\mathbf{x}} \left\{ \frac{4}{3} \cos\left[\frac{\pi}{a}\left(\frac{1}{3}, 0, 1\right) \cdot \mathbf{r}_i\right] - \frac{1}{3} \cos\left[\frac{\pi}{a}(0, 1, 0) \cdot \mathbf{r}_i\right] \right\} \ , \qquad (B1)$$

where $2a$ is the lattice constant. However, a similar result would also be obtained using

$$\mathbf{S}_i \propto \hat{\mathbf{x}}\left\{\frac{2}{3}\cos\left[\frac{\pi}{a}\left(\frac{1}{3},1,0\right)\cdot\mathbf{r}_i\right] + \frac{2}{\sqrt{3}}\sin\left[\frac{\pi}{a}\left(\frac{1}{3},0,1\right)\cdot\mathbf{r}_i\right]\right.$$

$$\left. + \frac{1}{3}\cos\left[\frac{\pi}{a}\left(0,0,1\right)\cdot\mathbf{r}_i\right]\right\}. \tag{B2}$$

The results of Ref. 1 show that in the experimentally observed magnetic structure the Fourier amplitude vector $\mathbf{S}(\mathbf{q})$ is parallel with the $\frac{1}{3}$ component of the wave vector $\mathbf{q}$; i.e., the easy axis is along the $\frac{1}{3}$ direction; otherwise especially the $(\frac{7}{3},1,0)$ Bragg reflection would have a much stronger relative intensity.

The direction of the easy axis is readily understood because the orientations of the modulation vectors $\mathbf{S}[(\pi/a)(\frac{1}{3},1,0)] \parallel \hat{\mathbf{x}}$ and $\mathbf{S}[(\pi/a)(0,0,1)] \perp \hat{\mathbf{z}}$ minimize the dipole-dipole energy among the structures with $(\pi/a)(\frac{1}{3},1,0)$ and $(\pi/a)(0,0,1)$ modulations, respectively.

In principle, it is also possible that the spin configuration is a multi-k structure, obtained by superposing two or three independent modulations with perpendicular $\frac{1}{3}$ directions. No direct coupling can, however, exist between these, because (e.g.) vectors $(\frac{1}{3},0,1)$ and $(0,\frac{1}{3},1)$ do not differ by $\mathbf{K}_m$'s of the pyrite structure. Coupling can be present only between Fourier components which have the same $\frac{1}{3}$ axis: These have parallel amplitudes $\mathbf{S}(\mathbf{q})$ according to neutron-diffraction data. We note that the DM energy is necessarily zero for allowed structures, and it is thus likely that the DM coupling does not stabilize the spin configuration observed in MnSe$_2$.

In the isotropic Heisenberg model, $\mathcal{H} = \sum_{i>j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$, the ordering is determined by minimizing $\gamma(\mathbf{q}) = \sum_j J_{ij}\exp(i\mathbf{q}\cdot\mathbf{r}_{ij})$. With only antiferromagnetic nearest-

neighbor interaction $J_1 > 0$, function $\gamma(\mathbf{q})$ is minimized when $\mathbf{q} = (\pi/a)(1,x,0)$. We note that

$$\gamma[\mathbf{q} = (\pi/a)(1,x,0)] = c_0 + c_2\cos 2\pi x + c_4\cos 4\pi x + \cdots, \tag{B3}$$

because, by the symmetry of $\gamma(\mathbf{q})$ at the boundary of the first Brillouin zone, this function is even with respect to x at $x = 0$ and $x = \frac{1}{2}$. In order to place the minimum at $x = \frac{1}{3}$, it is necessary to have $c_2 = 2c_4 > 0$. The simplest way to achieve this is to include next-nearest-neighbor $[\mathbf{r}_{ij} = a(2,0,0)]$ and eighth-nearest-neighbor $[\mathbf{r}_{ij} = a(4,0,0)]$ exchange. This result remains unchanged when one admits anisotropic interactions allowed in ideal fcc systems. It also turns out to be impossible to set the minimum at $x = \frac{1}{3}$ by using the infinite range magnetic dipole-dipole interaction and next-nearest-neighbor exchange.

In practice it is impossible that the minimum of $\gamma(\mathbf{q})$ is exactly at $\mathbf{q} = (\pi/a)(1,\frac{1}{3},0)$. Lock-in effects, however, owing to the tendency to "square up" the spin structure so that sublattice magnetizations are equal, will favor commensurate structures.[24,18]

Because thermal as well as quantum-mechanical fluctuations favor collinear spin configurations, we conclude that the ordering observed in MnSe$_2$ would result for coupling constants (e.g.) $J_1 \gg J_2 \approx 2J_8 > 0$ and when a small dipolar anisotropy is present.

An alternative possibility to explain the magnetic structure of MnSe$_2$ is to invoke four-spin exchange interactions.[13]

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