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Symmetric and antisymmetric anisotropic exchange energies as crucial factors for the magnetic structures in MnP, FeP, CrAs and MnAs

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Abstract. The isotropic and anisotropic exchange energies in phosphide and arsenide compounds with helical or ferromagnetic structures have been studied by means of an anisotropic two-band model. The anisotropic term is separated into a symmetric and an antisymmetric contribution. It appears that, in crystals with non-vanishing spin-orbit interaction, a circular isotropic helix minimizes the antisymmetric contribution (AEI) to the exchange energy. The helix is stable if the AEI compensates for the increase in the symmetric anisotropic energy that the deviation from a non-collinear spin arrangement causes. The band model predicts the correct ground state, with the exception of MnP, where the helical (ground state) and the ferromagnetic (high-temperature phase) configurations correspond to the same energy. The results confirm that the AEI and the shape of the Fermi surface are crucial for the stability of a helical magnetic structure.

1. Introduction

The magnetic phase diagram of $\text{Mn}_{1-x}\text{P}_y\text{Cr}_x\text{As}_{1-y}$ and its compounds, i.e. MnP, FeP, CrAs and MnAs, has been intensively studied for about two decades [1, 2]. From experimental investigations it is well established that several magnetic transitions between different helical and ferromagnetic phases take place [2]. For example, the magnetic structures in MnP can be separated into a double-helical low-temperature phase and a ferromagnetic high-temperature phase (table 1) [3]. For FeP and CrAs, which belong to the same orthorhombic space group (*Pnma*) as MnP, the helical structure is stable in the entire temperature range [4, 5]. On the other hand, MnAs corresponds to a ferromagnetic spin configuration and a crystal structure of NiAs type.

Several theoretical investigations mainly on the binary phosphide and arsenide compounds from $\text{Mn}_{1-x}\text{P}_y\text{Cr}_x\text{As}_{1-y}$ have been published [2, 5, 6]. For example, the exchange interaction has been studied by Kallel *et al* [5] and recently by Dobrzynski *et al* [2]. By using a localized Heisenberg Hamiltonian and group theory, Kallel *et al* [5] find that a stable helix exists only if the antisymmetric exchange interaction (AEI) from the spin-orbit interaction is extremely strong, particularly in CrAs. By assuming that the exchange interaction is long-ranged, Dobrzynski *et al* [2] show that this, not very realistic, result can be avoided. More precisely, Dobrzynski *et al* [2] find that the AEI is

Table 1. Transition temperatures for the helical (T_N) and the ferromagnetic (T_C) phase. Magnetic moments μ and spin propagation vectors q multiplied by twice the lattice parameter in the z direction for MnP, CrAs and FeP. Experimental results from [3–5].

Compound	T_N (K)	T_C (K)	μ (μ_B)	$q_z 2z$ (deg)
MnP	46	291	1.3	15.8
CrAs	280	—	2.1	60.8
FeP	125	—	0.41	28.5

necessary to establish a helix in CrAs. The occurrence of a spiral in MnP and FeP can, on the other hand, be understood within an isotropic Heisenberg model.

A shortcoming in these investigations is that they are based on a localized Heisenberg Hamiltonian, which does not take the conduction electrons into consideration in an appropriate way.

In spite of the fact that the physical reason for the complex magnetic structures is not known in detail, it is well established that, for instance, the mechanism is different for the transition metals and the rare earths. For itinerant magnetic systems, such as the 3d metals, band properties and the shape of the Fermi surface play an important role (so-called nesting) [7, 8]. Of vital importance also is the anisotropic exchange interaction [9–11]. In general, this interaction consists of a symmetric (SEI) and an antisymmetric (AEI) term. The SEI is the traditional anisotropy and has several origins, which in principle are present in all solids. The AEI, on the other hand, occurs only in crystals with low symmetry, and its origin is the spin-orbit interaction [10, 11]. Theoretical and experimental investigations have shown that the AEI favours the establishment of the helical structure in, for example, $Fe_{1-x}Co_xSi$ [12], $CsCuCl_3$ [13] and $MnSi$ [14].

The purpose of this paper is to study, by means of an anisotropic band model, whether the SEI and AEI or the isotropic exchange interaction is the crucial factor for the stability of the competing magnetic structures in MnP, FeP, CrAs and MnAs. We will also get an opportunity to compare the results from a band model and a Heisenberg model.

2. Basic theory

In order to study the magnetic energy in a multiphase magnetically ordered system, the q -dependent susceptibility tensor $\chi(q)$ is a very useful quantity, since its maximum value corresponds to the lowest exchange energy. A peak in $\chi(q)$ at $q = 0$ would then mean ferromagnetism, and one at some other q would indicate a helix, spin-density wave (SDW) or a more complicated arrangement of the magnetic moments and with a period defined by that wavevector q .

The general expression for $\chi(q)$ is too complicated to use in theoretical studies and one has to invoke approximations. The most common approach is the electron-gas approximation, and for several special cases $\chi(q)$ can be calculated. This holds for the Hartree-Fock approximation [15] and its correlated extension (i.e. random-phase approximation (RPA)) for band theory [16–20].

Common to almost all of these theoretical studies of the susceptibility is that one treats the tensor $\chi(q)$ as a scalar quantity. For the systems of interest here, the Fermi

surfaces are probably very anisotropic, and consequently the non-diagonal elements of the $\chi(q)$ matrix are not negligible.

We will therefore use the anisotropic q -dependent band model according to Sjöström [21]. It is based upon the approximation that the exchange and spin-orbit interactions can be treated as perturbations of a non-magnetic Hamiltonian. This leads to a Hamiltonian that is not diagonal with respect to the spin-orbit term. The diagonalization results in an exchange energy and a susceptibility matrix that depend on the orbital angular momentum vector. By assuming that the magnetization from the exchange interaction is related to a linear response function, and applying second-order perturbation theory, the following expression for the magnetic energy was obtained in [21]:

$$\epsilon_{\text{mag}}(q) = \sum_{G,G'} \sum_{i,j} V_{\text{ex},G} V_{\text{ex},G'}^* S_{G,i}(q) \chi^{-1}(q)_{GG',ij} S_{G',j}^*(q). \quad (1)$$

Here $V_{\text{ex},G}$ and $S_{G,i}(q)$ are the Fourier components of the local exchange potential and the spin density; $S_{G,j}(q)$ has the explicit form:

$$S_{G,j}(q) = (1/V) \int S(r) \exp\{i[q_i \cdot (R_n + \rho) + \rho \cdot G]\} dr. \quad (2)$$

Further in (1), the summations are over reciprocal lattice vectors G, G' and space coordinate directions ($i, j = x, y, z$).

The susceptibility tensor consists of an isotropic (χ^{IS}) term from the exchange interaction and an anisotropic term (χ^{AN}) arising from the exchange interaction and indirectly from the spin-orbit interaction via the unitary diagonalization matrix U_K given in [21]. Thus we have

$$\chi(q)_{GG',ij} = \chi(q)_{GG'}^{\text{IS}} \delta(i, j) + \chi(q)_{GG'}^{\text{AN}}. \quad (3)$$

Here

$$\begin{aligned} \chi(q)_{GG'}^{\text{IS}} &= \sum_{k'} \sum_k F_G(k, k', k - q, k' + q) F_{G'}(k, k', k - q, k' + q)^* \\ &\times \frac{f(\epsilon_F - \epsilon_k) f(\epsilon_F - \epsilon_{k'}) f(\epsilon_{k-q} - \epsilon_F) f(\epsilon_{k'+q} - \epsilon_F)}{\epsilon_{k-q} + \epsilon_{k'+q} - \epsilon_k - \epsilon_{k'}} \end{aligned} \quad (4)$$

and

$$\begin{aligned} \chi(q)_{GG',ij}^{\text{AN}} &= \sum_{\substack{s, s' \\ s'', s'''}} \sum_{k, k'} \Lambda_{GG', ss' s'' s'''}(k, k', k - q, k' + q) \langle s'' | U_{k-q} \sigma(1)_i U_k^{-1} | s \rangle \\ &\times \langle s | U_k \sigma(1)_j U_k^{-1} | s'' \rangle \langle s' | U_{k'+q} \sigma(2)_i U_{k'+q}^{-1} | s''' \rangle \langle s''' | U_{k'+q} \sigma(2)_j U_{k'+q}^{-1} | s' \rangle \end{aligned} \quad (5)$$

where

$$\begin{aligned} \Lambda_{GG', ss' s'' s'''}(k, k', k - q, k' + q) &= (\mu_B / \Omega) F_G(k, k', k - q, k' + q) F_{G'}(k, k', k - q, k' + q)^* \\ &\times \left(\frac{f(\epsilon_F - \epsilon_k + sL_k) f(\epsilon_F - \epsilon_{k'} + s'L_{k'})}{\Delta\epsilon + s''L_{k-q} + s'''L_{k'+q} - sL_k - s'L_{k'}} \right. \\ &\times \frac{f(\epsilon_{k-q} - s''L_{k-q} - \epsilon_F) f(\epsilon_{k'+q} - s'''L_{k'+q} - \epsilon_F)}{\Delta\epsilon + s''L_{k-q} + s'''L_{k'+q} - sL_k - s'L_{k'}} \\ &\left. - \frac{f(\epsilon_F - \epsilon_k) f(\epsilon_F - \epsilon_{k'}) f(\epsilon_{k-q} - \epsilon_F) f(\epsilon_{k'+q} - \epsilon_F)}{\Delta\epsilon} \right). \end{aligned} \quad (6)$$

Here $F_G(k, k', k - q, k' + q)$ is the Fourier transform of the wavefunction, and $f(x)$ is the Fermi distribution function, i.e. $f(x) = 1$ for $x > 0$ and 0 for $x < 0$ then $T = 0$. Further ε_F is the Fermi energy, $\Delta\varepsilon = \varepsilon_{k-q} + \varepsilon_{k'+q} - \varepsilon_{k'} - \varepsilon_k$. In general, the states k , k' , $k - q$ and $k' + q$ belong to different bands. For brevity, however, the band indices have been suppressed in the expressions above. In (5), the summation is over all spin states that conserve the initial spins ($s + s' = s'' + s'''$).

The non-diagonal matrix elements of the susceptibility tensor (or its inverse) can be separated into a symmetric ($\chi_{\alpha\beta}^S = \chi_{\beta\alpha}^S$, $\alpha\beta = x, y, z$) and an antisymmetric term ($\chi_{\alpha\beta}^{AS} = -\chi_{\beta\alpha}^{AS}$). This means that the spin-dependent factors in the anisotropic energy expression (1) can also be separated in a symmetric and an antisymmetric term as follows:

$$\begin{aligned} \varepsilon_{\alpha\beta} &= \chi_{\alpha\beta}^{-1} S_{\alpha q} S_{\beta q}^* + \chi_{\beta\alpha}^{-1} S_{\beta q} S_{\alpha q}^* = [(\chi_{\alpha\beta}^{-1})^S + (\chi_{\alpha\beta}^{-1})^{AS}] S_{\alpha q} S_{\beta q}^* + [(\chi_{\beta\alpha}^{-1})^S + (\chi_{\beta\alpha}^{-1})^{AS}] S_{\beta q} S_{\alpha q}^* \\ &= (\chi_{\alpha\beta}^{-1})^S (S_{\alpha q} S_{\beta q}^* + S_{\beta q} S_{\alpha q}^*) + (\chi_{\alpha\beta}^{-1})^{AS} (S_{\alpha q} S_{\beta q}^* - S_{\beta q} S_{\alpha q}^*) \end{aligned} \quad (7)$$

(for brevity q is here an index and G and G' are omitted).

The relation (7) can also be written in operator form as

$$H = S_q J(q) S_q^* + D(q) \cdot (S_q \times S_q^*). \quad (8)$$

For comparison with the Heisenberg Hamiltonian we have in (8) introduced the abbreviations $J(q)$ and $D(q)$, which correspond to the symmetric and antisymmetric tensors of χ^{-1} .

In order to proceed we need explicit symmetric and antisymmetric expressions of the susceptibility. In [21], the non-diagonal susceptibility in (3) is separated into an antisymmetric (AS) and a symmetric (S) in the following way:

$$\begin{aligned} \chi_{GG',ij}^{AS}(q) &= iA(i,j) \left[\sum_{\text{bands } k,k'} \sum (\Lambda_{GG',i-1-1-11} + \Lambda_{GG',-11-11}) \right. \\ &\quad \times (L_{(k-q)n}/L_{k-q} + L_{(k)n}/L_k)(L_{(k'+q)n}/L_{k'+q} + L_{(k')n}/L_{k'}) \\ &\quad \times \sum_{\text{bands } k,k'} \sum (\Lambda_{GG',1111} + \Lambda_{GG',-1-1-1-1}) (L_{(k-q)n}/L_{k-q} - L_{(k)n}/L_k) \\ &\quad \left. \times (L_{(k'+q)n}/L_{k'+q} - L_{(k')n}/L_{k'}) \right] \end{aligned} \quad (9)$$

and

$$\begin{aligned} \chi_{GG',ij}^S(q) &= \sum_{\text{bands } k,k'} \sum (\Lambda_{GG',1111} + \Lambda_{GG',-1-1-1-1} + \Lambda_{GG',1-1-11} + \Lambda_{GG',-11-11}) \\ &\quad \times \left(\delta(i,j) + \frac{L_{ki} L_{k'j} L_{(k-q)i} L_{(k'+q)j}}{L_k L_{k'} L_{k-q} L_{k'+q}} \right. \\ &\quad \left. + \frac{L_{kj} L_{k'i} L_{(k-q)j} L_{(k'+q)i} - (L_{k-q} \cdot L_k)(L_{k'+q} \cdot L_{k'}) \delta(i,j)}{L_k L_{k'} L_{k-q} L_{k'+q}} \right). \end{aligned} \quad (10)$$

Here i, j, n are space coordinate indices x, y or z , $\Lambda_{GG',ss's''s'''}$ is given in expression (6), and $A(i, j)$ is the antisymmetric tensor ($A(i, j) = 1$, $A(j, i) = -1$ and $A(i, i) = 0$). Note also that the n coordinate in (9) is directed perpendicular to the spins. It is therefore obvious that the AEI expression (9) vanishes if the n component of L_k is 0 (see also (6)).

We will, in section 4, utilize (9) and (10) to calculate the AEI and SEI.

3. General anisotropic properties of a helix and a spin-density wave

In this section we show that a helix and a SDW correspond to completely different AEI and SEI. In order to do this, we write down the Fourier transform for a general spin density.

$$S(\mathbf{R}_n + \boldsymbol{\rho})_\alpha = \sum_G \sum_q S_{G,\alpha}(\mathbf{q}) \exp\{i[\mathbf{q} \cdot (\mathbf{R}_n + \boldsymbol{\rho}) + \boldsymbol{\rho} \cdot \mathbf{G}]\} \quad (11)$$

where $\boldsymbol{\rho}$ is a distance vector in the unit cell n .

We will consider the case when $S_{G,\alpha}(\mathbf{q})$ can be separated into one part that describes a circular plane helix ($S_{G,\alpha}^H(\mathbf{q})$) and another part that describes a sinusoidal spin-density wave ($S_{G,\alpha}^{SDW}(\mathbf{q})$). For this case we assume that (11) has the form

$$\begin{aligned} S(\mathbf{R}_n + \boldsymbol{\rho})_\alpha &= \sum_G \sum_q [S_{G,\alpha}^H(\mathbf{q}_n) + S_{G,\alpha}^{SDW}(\mathbf{q}_m)] \exp\{i[\mathbf{q} \cdot (\mathbf{R}_n + \boldsymbol{\rho}) + \boldsymbol{\rho} \cdot \mathbf{G}]\} \\ &= \sum_G \sum_q \{a_n(\mathbf{u} + i\mathbf{v}) \exp[i\Phi(\mathbf{q}_n)] + b_m \mathbf{w} \sin(\mathbf{q}_m \cdot \mathbf{r} + \phi_m)\} \\ &\quad \times \exp\{i[\mathbf{q}_m \cdot (\mathbf{R}_m + \boldsymbol{\rho}) + \boldsymbol{\rho} \cdot \mathbf{G}]\} \end{aligned} \quad (12)$$

where a_n and b_m are constants and \mathbf{u} , \mathbf{v} , \mathbf{w} are normalized vectors, directed in such a way that \mathbf{v} and \mathbf{u} are orthogonal to each other. Further in (12) $\Phi(\mathbf{q}) = \mathbf{r} \cdot \mathbf{q} + \phi_0$ (ϕ_0 is the reference phase angle).

Let us investigate a spin component oriented in the \mathbf{uv} plane making the angle Φ with the \mathbf{u} axis (e.g. a helix):

$$S_{\alpha q} = (1/2)(u_\alpha \cos \Phi - v_\alpha \sin \Phi) + (i/2)(u_\alpha \sin \Phi + v_\alpha \cos \Phi). \quad (13)$$

For the general case when different spin components $S_{\alpha q}$ and $S_{\beta q}$ correspond to different reciprocal vectors with, say, indices n and m , one obtains the following expression for the spin product terms in (7):

$$\begin{aligned} S_{\alpha q} S_{\beta q}^* + S_{\beta q} S_{\alpha q}^* &= (1/2)[(u_\alpha u_\beta + v_\alpha v_\beta) \cos(\Phi_m - \Phi_n) \\ &\quad + (u_\alpha v_\beta - v_\alpha u_\beta)] \sin(\Phi_m - \Phi_n) \end{aligned} \quad (14)$$

and

$$\begin{aligned} S_{\alpha q} S_{\beta q}^* - S_{\beta q} S_{\alpha q}^* &= -(i/2)[(u_\alpha v_\beta - v_\alpha u_\beta) \cos(\Phi_m - \Phi_n) \\ &\quad + (u_\alpha u_\beta + v_\alpha v_\beta)] \sin(\Phi_m - \Phi_n). \end{aligned} \quad (15)$$

Here we have used (13). By inserting the relations between u_α , v_β , v_α and u_β , we easily find that the first term in (14) and the second term in (15) are equal to zero for a helix of a type given by (13) in the $\alpha\beta$ plane (independently of the orientation of the orthogonal unit vectors \mathbf{u} , \mathbf{v}). On the other hand, the antisymmetric expression $u_\alpha v_\beta - v_\alpha u_\beta$ assumes its extreme value for the same type of helix. The contributions from the terms with Φ_m and Φ_n corresponding to different reciprocal vectors cancel to a large extent in the lattice summation. In the first-order approximation, (14) and (15) thus include only the term with $G_m = G_n = 0$, and we can write

$$S_{\alpha q} S_{\beta q}^* + S_{\beta q} S_{\alpha q}^* = (1/2)(u_\alpha u_\beta + v_\alpha v_\beta) \quad (16)$$

$$S_{\alpha q} S_{\beta q}^* - S_{\beta q} S_{\alpha q}^* = -(i/2)(u_\alpha v_\beta - v_\alpha u_\beta). \quad (17)$$

Substituting (16) and (17) in the energy expression (1), we easily find that the spin

distribution given by the helical term in (12) minimizes the energy contribution from the AEI and gives a vanishing diagonal symmetric exchange if the spin distribution corresponds to a circular isotropic helix.

The expressions for the SDW are to first-order approximation

$$S_{\alpha q} S_{\beta q}^* + S_{\beta q} S_{\alpha q}^* = w_\alpha w_\beta \sin(\mathbf{q}_n \cdot \mathbf{r} + \Phi_n) \quad (18)$$

$$S_{\alpha q} S_{\beta q}^* - S_{\beta q} S_{\alpha q}^* = 0. \quad (19)$$

By inserting (18) in (1) we find that a SDW minimizes the symmetric anisotropic energy (SEI) contribution, i.e. opposite to the helical case.

A ferromagnetic structure always has the lowest anisotropic energy due to alignment of the spins in the 'easy' direction. This means that the diagonal terms in (1) minimize the energy while the non-diagonal terms vanish for ferromagnetism. A criterion for a stable helix is thus that the AEI does not vanish (for symmetry reasons) but compensates for the increase in the symmetric anisotropic energy that the deviation from a non-collinear spin arrangement causes.

4. Isotropic and anisotropic exchange energy in MnP, FeP, CrAs and MnAs

4.1. Exchange interaction

By using energy bands and wavefunctions from linear muffin-tin orbital (LMTO) calculations and the itinerant model presented in section 2, combined with the symmetry arguments in section 3, we will now derive expressions for the different contributions to the exchange energy for the helical, the SDW and the ferromagnetic structures.

Since the isotropic contributions of the exchange energy can be treated as a rather simple special case of the anisotropic one, we start with the latter.

According to expression (1), the difference in anisotropic energy between ferromagnetism (with the spins directed along the c axis) and helimagnetism (spins in the ab plane) with $\mathbf{q} = \mathbf{q}_h$ is, with x as the reference spin direction, for MnP, FeP and CrAs,

$$\begin{aligned} \varepsilon_{\text{an}}(\text{ferro}) - \varepsilon_{\text{an}}(\text{helix}) &= \sum_{G, G'} V_{\text{ex}, G'} V_{\text{ex}, G}^* \{ S_{G,z}^*(\mathbf{q} = 0) \chi^{-1}(\mathbf{q} = 0)_{GG',zz} S_{G',z}(\mathbf{q} = 0) \\ &\quad - \chi^{-1}(\mathbf{q}_h)_{GG',xy} [S_{G,x}(\mathbf{q}_h) S_{G',y}^*(\mathbf{q}_h) - S_{G,y}(\mathbf{q}_h) S_{G',x}^*(\mathbf{q}_h)] \\ &\quad - S_{G,x}(\mathbf{q}_h) \chi^{-1}(\mathbf{q}_h)_{GG',xz} S_{G',x}^*(\mathbf{q}_h) \}. \end{aligned} \quad (20)$$

Here we have also used (7) and the fact that the angular momentum vector L_k is directed perpendicular to the mirror plane ab . The latter circumstance is a symmetry property of the space group $Pnma$ and can be obtained either from the expression for L_k [22],

$$L_k = -(i\hbar/4m^2c^2) \int \psi_k(\mathbf{r})^* [\nabla V(\mathbf{r}) \times \nabla] \psi_k(\mathbf{r}) d\mathbf{r} \quad (21)$$

or by group-theoretical treatments of the spin configurations and the Dzyaloshinski-Moriya (DM) vector in $Pnma$ [5]. We note in (20) that the ferromagnetic phase and the hypothetical SDW is purely symmetric while the helix is both symmetric and anti-symmetric.

In the appendix, we show that the energy expression (20) is an approximately linear function of χ and can be written in the more handy form:

$$\begin{aligned} \epsilon_{\text{an}}(\text{ferro}) - \epsilon_{\text{an}}(\text{helix}) = & \sum_{G, G'} C_{GG'}(T) [\chi_{GG',zz}(0) \langle S_{G,z}(0) \rangle \langle S_{G',z}^*(0) \rangle - \chi_{GG',xy}^{\text{AS}}(\mathbf{q}) \\ & \times \langle S_{G,x}(\mathbf{q}) \rangle \langle S_{G',y}^*(\mathbf{q}) \rangle \sin(\mathbf{q} \cdot \mathbf{R}) - \chi_{GG',xx}^{\text{SY}}(\mathbf{q}) \langle S_{G,x}(\mathbf{q}) \rangle \langle S_{G',x}^*(\mathbf{q}) \rangle \cos(\mathbf{q} \cdot \mathbf{R})] \end{aligned} \quad (22)$$

where the constant, $C_{GG'}(T)$, is directly proportional to the magnetic transition temperature (see the appendix). The $\langle S_{G,i}(\mathbf{q}) \rangle$ are the mean value of the spin defined in the appendix (equation (A6)). Furthermore, in (22) the summations are restricted to first- and second-order terms, i.e. G and G' are equal to 0 and 1.

If we replace the ferromagnetic structure with a SDW propagating along the z axis, we obtain in the same way

$$\begin{aligned} \epsilon_{\text{an}}(\text{SDW}) - \epsilon_{\text{an}}(\text{helix}) = & \sum_{G, G'} C_{GG'}(T) [\chi_{GG',zz}(\mathbf{q}) \langle S_{G,z}(\mathbf{q}) \rangle \langle S_{G',z}^*(\mathbf{q}) \rangle \\ & - \chi_{GG',xy}^{\text{AS}}(\mathbf{q}) \langle S_{G,x}(\mathbf{q}) \rangle \langle S_{G',y}^*(\mathbf{q}) \rangle \sin(\mathbf{q} \cdot \mathbf{R}) \\ & - \chi_{GG',xx}^{\text{SY}}(\mathbf{q}) \langle S_{G,x}(\mathbf{q}) \rangle \langle S_{G',x}^*(\mathbf{q}) \rangle \cos(\mathbf{q} \cdot \mathbf{R})]. \end{aligned} \quad (23)$$

The explicit expression for the susceptibilities in (22) and (23) according to (9) and (10) is

$$\chi_{GG',zz}(\mathbf{q}) = 2 \sum_{\text{bands } k, k'} \Lambda^{\text{TOT}}(\mathbf{q}) \quad (24)$$

where

$$\Lambda^{\text{TOT}}(\mathbf{q}) = \Lambda(\mathbf{q})_{GG',1111} + \Lambda(\mathbf{q})_{GG',-1-1-1-1} + \Lambda(\mathbf{q})_{GG',1-1-11} + \Lambda(\mathbf{q})_{GG',-11-11} \quad (25)$$

$$\chi(\mathbf{q})_{GG',xy}^{\text{AS}}(\mathbf{q}) = 4i \sum_{\text{bands } k, k'} \sum [\Lambda(\mathbf{q}_h)_{GG',1-1-11} + \Lambda(\mathbf{q}_h)_{GG',-11-11}] \quad (26)$$

and

$$\chi(\mathbf{q})_{GG',xx}^{\text{SY}}(\mathbf{q}) = \sum_{\text{bands } k, k'} \sum \Lambda^{\text{TOT}}(\mathbf{q}) [1 - ((L_{k-q} \cdot L_k)(L_{k'+q} \cdot L_{k'}) L_k L_{k'} L_{k-q} L_{k'+q})]. \quad (27)$$

As can be seen from the expressions (9) and (10), we have in (26) and (27) neglected terms that are smaller than the numerical inaccuracy.

4.2. Technical details in the calculations

Since experimental values of the magnetic moments, the \mathbf{q} -vectors and the transition temperatures are available [3-5] and L_k as well as the band structure can be calculated by standard methods, numerical values of all the quantities in section 4.1 can be obtained. In order to perform this computation the following methods and approximations have been used.

The band-structure calculations were performed using a self-consistent LMTO method. Relativistic effects are included except for the spin-orbit interaction of the band electrons. For the generation of the potential the local-density approximation with Gunnarsson-Lundqvist parametrization was adopted. The calculations were made for

Table 2. The various contributions to the calculated exchange energy (meV) for the magnetic structures in section 3. Abbreviations: SAE = symmetric anisotropic exchange energy, AAE = antisymmetric anisotropic exchange energy, AE = total anisotropic exchange energy, IE = isotropic exchange energy and $\Delta\varepsilon$ = total energy difference relative to the experimental ground state. The numerical inaccuracy for the energy differences is estimated to be ± 5 meV between ferromagnetism and helix or SDW, ± 2 between helix and SDW (lower because the susceptibilities are calculated for the same q -vector). The absolute values have much larger inaccuracy.

		SAE (meV)	AAE (meV)	AE (meV)	IE (meV)	$\Delta\varepsilon$ (meV)
MnP	Helix	-3	-8	-11	-442	0
	SDW	-8	0	-8	-442	3
	Ferrom.	-19	0	-19	-436	-2
FeP	Helix	-2	-7	-9	-192	0
	SDW	-7	0	-7	-192	2
	Ferrom.	-11	0	-11	-180	10
CrAs	Helix	-5	-16	-21	-432	0
	SDW	-15	0	-15	-432	6
	Ferrom.	-19	0	-19	-420	14
MnAs	Helix	-7	0	-7	-589	15
	SDW	-17	0	-17	-589	5
	Ferrom.	-21	0	-21	-590	0

the equilibrium volume of the orthorhombic structure with four atoms per unit cell and for 1428 k -points in the irreducible wedge of the Brillouin zone. The way to relate the potential to the local spin-density approximation (LSDA) is presented in [21]. The utilization of the LSDA to complex antiferromagnetic systems is motivated by the fact that self-consistent band calculations, including anisotropy, for systems with non-collinear magnetic structures, have been successfully performed by e.g. Kübler *et al* [23].

It appears that there are five bands, i.e. eigenvalues $\varepsilon(k)$, which cross the Fermi level in such a way that so-called nesting effects in principle are possible. Among these bands the different combinations of two-band systems have been selected in the computing of the susceptibility matrix. Inter- and well as intra-band interactions have been taken into account while excitations involving more than two bands have been neglected. The summations over k and k' are performed over the same k -mesh of the irreducible part of the Brillouin zone as for the band calculation. The q -vectors of the helix have been set equal to that k -point which deviates least from the experimental one, i.e. no interpolation between the k -points was performed.

The crucial point in such a calculation is the self-energy represented by $\Lambda(q_h)_{GG',ss's''}$ in (6), because it involves energy differences in the denominators, which can be very small. We have approached this problem by using a much finer mesh in the k -space than for ordinary band calculations. In this way we obtain high convergence for the Fermi level and the energy bands.

4.3. Results

The results of the numerical calculations are presented in table 2. We obtain the correct ground states for FeP, MnAs and CrAs. For MnP the ferromagnetic spin configuration has the lowest energy. The difference from the experimental helical structure is, however, so small that it is within the numerical uncertainty.

These results are mainly a consequence of the fact that the matrix elements of the susceptibility tensor, due to band crossing effects at the Fermi level, assume a lower value for $q = q_h$ than for $q = 0$. It is interesting to note that for $q = q_h$ inter-band transitions give a larger contribution to the matrix elements than intra-band transitions while the reverse condition is valid for $q = 0$. The dispersion relation of L_k also favours the antisymmetric term, particularly for CrAs.

It also turns out from table 2 that the total anisotropic energy varies from about 5% (CrAs) to 2% (MnP) of the total exchange energy.

The values of the uncertainty presented in table 2 of the energy difference include only the numerical inaccuracy, i.e. we have not taken into consideration the errors from the approximations involved in the method.

5. Conclusions

The model reproduces the magnetic ground state astonishingly well. The rather high numerical accuracy in this not very sophisticated computational study seems to be a consequence of the fact that the systematic errors cancel to a large extent in the subtraction in (22) and (23). In order to test the reliability of the susceptibility calculations, the author is planning to investigate if $\chi(q)$ in fact assumes a peak for the experimental q -vector. Such a calculation is meaningful only if it is based on an interpolation in the k -mesh.

Concerning the results of the arsenides the anisotropic energy, or more precisely the antisymmetric part, is the determining factor for the stability of the magnetic structure. But the AEI acts completely differently in the two systems; in MnAs the AEI vanishes (for symmetry reasons) and in CrAs it lowers the energy.

In FeP and MnP the AEI is small but crucial for the energy difference between the helix and the SDW. The transition to the ferromagnetic phase in MnP at $T = 48$ K can be understood, in the light of the small energy difference between the two magnetic phases in MnP, as a thermal change of the exchange interactions. This explanation is also compatible with the possibility of disturbing the spiral by an external field and in such a way to obtain a Lifshitz triple point [24].

Concerning the discussions of the ratio between the isotropic and anisotropic energy, this study supports the conclusions of Dobrzynski *et al* [2]. In fact it seems remarkable that a band model and an appropriate investigation based on the localized Heisenberg model can give such similar conclusions about the exchange interaction in the systems studied here.

Appendix. The exchange field approximation

Since time- and space-varying magnetic fields are generally quite small in magnetically ordered systems, a linear response theory is usually adequate [25]. If the band electrons

act as a linear medium, the susceptibility is independent of the effective magnetic field, and we may write [25]

$$S_{Gi}(\mathbf{q}) = 2\mu_B \sum_G \chi^*(\mathbf{q})_{GG'} \cdot_{ij} H_{G'}^{\text{eff}}(\mathbf{q}). \quad (\text{A1})$$

By inserting (A1) in (1) we obtain an energy expression that is directly proportional to the susceptibility:

$$\varepsilon_{\text{mag}}(\mathbf{q}) = \sum_{G,G'} \sum_{i,j} V_{\text{ex},G} V_{\text{ex},G'}^* H_{G'}^{\text{eff}}(\mathbf{q}) \chi^*(\mathbf{q})_{GG'} \cdot_{ij} H_{G'}^{\text{eff}}(\mathbf{q}). \quad (\text{A2})$$

In order to find a convenient expression for numerical calculations, we will use the exchange field theory.

The general exchange field approximation that follows is essentially a combination of those used by James *et al* [26] and Nagamiya [9]. In this approximation H^{eff} is defined as the thermal mean value of the magnetic field that an arbitrary atom experiences from all other atoms in the crystal. The physical origin of this field is the exchange interaction and the corresponding energy is the scalar product of the mean value of the spin (defined below) and the exchange field for the atom i :

$$\varepsilon_i^{\text{ex}} = \langle S_i \rangle \cdot H_i^{\text{ex}}. \quad (\text{A3})$$

The general form of the exchange field is assumed to be a sum over exchange integrals and spins:

$$H_i^{\text{ex}} = 2g_S \mu_B \sum_j J_{ij} \langle S_j \rangle + H^{\text{an}}. \quad (\text{A4})$$

Here the first term is isotropic and the second anisotropic. Since we have taken the anisotropy into account in the Hamiltonian, we neglect the second-order effect from H^{an} in (A4).

The thermal mean value of the spins can be obtained as follows. We consider a lattice of classical spins. The orientation of spin i will be denoted by Ω_i , representing the polar and the azimuthal angles of the spin direction, i.e. $\Omega_i(\phi, \theta)$. Let the distribution of the spin i be given by the normalized function $\rho_i(\Omega)$. The mean value of spin i can now be defined as

$$\langle S_i \rangle = \int S_i \rho_i(\Omega) d\Omega. \quad (\text{A5})$$

Further we denote the exchange energy between spins i and j by $\varepsilon_{ij}(\Omega_i, \Omega_j)$.

We are seeking that set of distribution functions which minimizes the Helmholtz free energy

$$F = U - TS. \quad (\text{A6})$$

Here the internal energy U and the entropy S are given by

$$U = (1/2) \sum_{i,j} \int d\Omega_i \rho_i(\Omega_i) \varepsilon_{ij}(\Omega_i, \Omega_j) \rho_j(\Omega_j) d\Omega_j \quad (\text{A7})$$

$$S = k_B \sum_i \int \rho_i(\Omega_i) \ln \rho_i(\Omega_i) d\Omega_i. \quad (\text{A8})$$

Minimization of the free energy with respect to all the ρ_i yields

$$\begin{aligned} \rho_i(\Omega_i) = \exp \left[\beta \sum_j \int \rho_j(\Omega_j) \varepsilon_{ij}(\Omega_i, \Omega_j) d\Omega_j \right] \\ \times \left\{ \int d\Omega_j \exp \left[\beta \sum_j \int \rho_j(\Omega_j) \varepsilon_{ij}(\Omega_i, \Omega_j) d\Omega_j \right] \right\}^{-1} \end{aligned} \quad (\text{A9})$$

Here $\beta = 1/k_B T$. By inserting (A9) in the expression for the mean value of spin (A5) and using (A3) we obtain

$$\langle S_i \rangle = \int S_i \exp(\beta S_i \cdot H_i^{\text{ex}}) d\Omega_i / \int \exp(\beta S_i \cdot H_i^{\text{ex}}) d\Omega_i. \quad (\text{A10})$$

In a quantum-mechanical system the spin S_i assumes a number of discrete thermally excited states. It is therefore convenient to replace the integrals in (A10) by a sum over the expectation values of the spin wavefunction, i.e. the trace (Tr) of S_i . That yields

$$\langle S_i \rangle = \text{Tr } S_i \exp(\beta S_i \cdot H_i^{\text{ex}}) / \text{Tr} \exp(\beta S_i \cdot H_i^{\text{ex}}). \quad (\text{A11})$$

At all temperatures (A11) has the solution $\langle S_i \rangle = 0$ representing the disordered state. As the temperature decreases, solutions with non-vanishing mean spin appears if the exchange interaction is sufficiently strong. These solutions correspond to ordered spin states.

By expanding the exponential of (A11) in powers of S_i we can, as a good approximation in the neighbourhood of a branching temperature, neglect all terms with the exception of the first and so obtain

$$\langle S_i \rangle = \beta(1/3)S(S+1)H_i^{\text{ex}} \quad (\text{A12})$$

with

$$H_i^{\text{ex}} = [3k_B T/S(S+1)]\langle S_i \rangle. \quad (\text{A13})$$

By inserting the Fourier transform of (A13) in (A2) and by using (A3) we obtain

$$\varepsilon_{\text{mag}}(\mathbf{q}) = \sum_{G,G'} \sum_{i,j} C_{GG'}(T) \langle S_{G,i}(\mathbf{q}) \rangle \chi^*(\mathbf{q})_{GG',ij} \langle 2S_{G',j}^*(\mathbf{q}) \rangle. \quad (\text{A14})$$

Here we have introduced the temperature-dependent constant given by

$$C_{GG'}(T) = V_{\text{ex},G} V_{\text{ex},G'}^* 3k_B T/S(S+1). \quad (\text{A15})$$

Note that $C_{GG'}(T)$ is independent of \mathbf{q} in this approximation.

Since expression (A14) has a simpler form than (A2), we will use it for studying the exchange energy. Finally we note that in the expressions (22) and (23) a sine term appears since the spins can be written as a vector (see (8)).

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