

Distinct Surface Phenomena in Magnets

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Abstract

We discuss several forms of surface effect in antiferromagnetic and ferromagnetic materials. We begin by introducing the Heisenberg exchange interaction model and show that the introduction of a surface boundary condition into this model can result in distinct behaviour in the surface region. We next discuss Dzyaloshinsky's symmetry arguments which explain the possibility of the existence of a ferromagnetic moment in an antiferromagnetic material and briefly discuss the microscopic theory developed by Moriya to describe the effect. The possibility of chirality being introduced by the anisotropic superexchange interaction proposed by Dzyaloshinsky and Moriya is then investigated and a model for the chiral energy in the surface region is given from phenomenological principles. The form of this energy is then found to depend upon a distribution function $\eta(z)$. By minimization of this chiral energy the z dependence of $\eta(z)$ is determined.

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1 Introduction

1.1 Magnetism

The magnetic properties of materials are determined by the quantum mechanical nature of the electrons within them. The intrinsic spin of an electron leads to a magnetic moment of an atom, which in turn leads to a force on the atom when placed inside a magnetic field, as shown in several experiments utilising the Stern-Gerlach effect. This magnetic moment is also important within materials even in the absence of an applied magnetic field, as the magnetic moments of neighbouring atoms interact with one another.

These inter-atomic interactions between neighbouring atoms can effectively be treated as an exchange field. This exchange interaction is particularly important for determining the behaviour of magnetic materials in ordered magnetic states. The model which is of interest here, concerning these ordered magnetic states is the Heisenberg model [8, p. 288].

1.2 Heisenberg Model

As has already been mentioned, magnetism is a quantum mechanical effect. The magnetic moment of a particle is proportional to its intrinsic spin. Therefore in order to model the interactions between the magnetic moments within matter it is necessary to form a model from quantum mechanical groundings. Since the electrons which are primarily responsible for the magnetic behaviour of materials are usually localised around atoms on a regular lattice, we will consider the simple case of two interacting localised electrons. The electrons are spin $1/2$ particles and are aligned either up or down with respect to the axis defined by

the applied magnetic field. It is possible to partially describe the system of two interacting electrons by the wavefunction $\psi(\vec{r}_1, \vec{r}_2)$ where \vec{r}_1 and \vec{r}_2 are the position vectors of the two electrons. In order to describe the total state of the system this spatial wavefunction must be multiplied by the spin eigenstates of the system. For this we must define a basis for these spin eigenstates. We will concern ourselves only with the eigenstates of the z component \hat{S}^z of the total spin operator \hat{S} . Our basis states are therefore

$$|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle. \quad (1.2.1)$$

This basis results in an eigenvalue for the z component of spin \hat{S}^z which is equal to the sum of the spins in the z direction. Since electrons are fermions it is not adequate to simply use the states given in (1.2.1) since if two fermions have their positions exchanged the wavefunction must transform in an antisymmetric manner. We therefore require that $\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1)$. The simplest normalised linear combination of the states given in (1.2.1) which conform to this additional condition are

$$\frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle], \quad (1.2.2a)$$

$$|\uparrow\uparrow\rangle, \quad (1.2.2b)$$

$$\frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle], \quad (1.2.2c)$$

$$|\downarrow\downarrow\rangle. \quad (1.2.2d)$$

The state shown in (1.2.2a) is antisymmetric since interchanging of the two electrons leads to minus the original state. This state is known as the singlet state of the electron pair and has total spin $S = 0$. The last three states are known collectively as the triplet state of the pair. All of the states shown in (1.2.2) are eigenstates of both the total angular momentum operator and the z component operator. The physical interpretation of the states is that the singlet state refers to an arrangement of electrons with spins aligned antiparallel and net total angular momentum $S^z = 0$, while the triplet state defines a situation where the spins of the electrons are aligned parallel to one another resulting in a net total angular momentum $S^z = 1$ [5, p. 105].

We now wish to find a relation between the spins of the system and the energy. In order to do this we define \hat{S}_1 as the spin operator acting on the first electron and \hat{S}_2 to be the spin operator acting on the second electron. We can now write

$$\hat{S} \cdot \hat{S} = (\hat{S}_1 + \hat{S}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \cdot \hat{S}_2, \quad (1.2.3)$$

where \hat{S} is the total spin operator for the system of two electrons. Since both electrons have spin $1/2$, the eigenvalues of \hat{S}_1^2 and \hat{S}_2^2 are identical and are given by $S(1+S) = (1/2)(1+1/2) = 3/4$. We can see that the eigenvalue of \hat{S}^2 is zero for the singlet state and one for the triplet state. We can therefore find the eigenvalues of \hat{S}^2 , which are $S(1+S) = 0$ for the singlet state and $1(1+1) = 2$ for the triplet state. Similarly we find that the eigenvalue S_{12} of $\hat{S}_1 \cdot \hat{S}_2$ is $-3/4$ for the singlet state and $1/4$ for the triplet state. From these eigenvalues and eigenstates we now derive an expression for the energy of the pair. The energy of the system can be written as follows

$$E = c - JS_{12}. \quad (1.2.4)$$

In this expression c and J are constants with J being known as the *exchange constant*. If we let the exchange constant J be equal to the difference in the energies of the possible states, therefore $J = E_{\text{singlet}} - E_{\text{triplet}}$. It is now possible to calculate c by noting that

when $S_{12} = -3/4$, $E = E_{\text{singlet}}$ and when $S_{12} = 1/4$, $E = E_{\text{triplet}}$. The energy can now be written as

$$E = \frac{1}{4}(E_{\text{singlet}} + 3E_{\text{triplet}}) - JS_{12}. \quad (1.2.5)$$

The first term of this equation is a constant and can therefore be ignored if the zero energy of the system is appropriately defined. The second term gives a convenient form of the interaction energy between two spins.

It is this form of interaction energy which is used in the Heisenberg model allowing the Hamiltonian of a magnetic system of interacting moments to be described by

$$\hat{H} = \sum_{i<j=1}^N J_{ij} \hat{S}_i \cdot \hat{S}_j + H \sum_{i=1}^N \hat{S}_i^z, \quad (1.2.6)$$

where \hat{H} is the Hamiltonian of the system, J is the exchange constant between sites i and j , the operators \hat{S}_i and \hat{S}_j are the spin operators of the neighbouring sites i and j with the sum over all of the nearest neighbour sites j to a given site i . The second term is concerned with an applied magnetic field H and its interaction with the z spin of the site i . If the exchange constant J is greater than 0 the neighbouring magnetic moments will tend to align antiparallel to each other and the material will be antiferromagnetic, in this phase the material will have no net magnetic moment. If J is less than zero then the neighbouring moments will tend to align parallel to one another creating a ferromagnetic state and leading to a net magnetic moment for the material even in the absence of an applied magnetic field [9, p. 341].

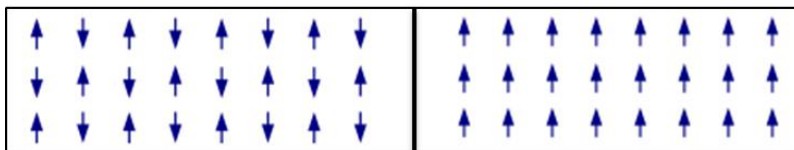


Figure 1: Left: Spin arrangement for exchange integral $J > 0$ (Antiferromagnet) Right: Spin arrangement for exchange integral $J < 0$ (Ferromagnet)

The Heisenberg model is quantum mechanical in nature as can be seen from the use of operators rather than vectors, it assumes that all interactions can be treated in terms of pairs of spins. This requires that the neighbouring sites must be spaced sufficiently such that the wavefunctions of neighbouring magnetic ions have little overlap. Despite the quantum mechanical nature of this model it is the aim of this study to treat the system quasi-classically. This means treating the spin operators as classical 3-component vectors, while this approach will be inadequate to achieve quantitatively accurate results the aim is to study the effects of a surface boundary condition on the direction of the magnetic moments near the surface and this approach is sufficient to obtain qualitative results regarding this. The quasi-classical model which will be used is

$$E = \sum_{i<j=1}^N J_{ij} \vec{S}_i \cdot \vec{S}_j + H \sum_{i=1}^N \vec{S}_i^z. \quad (1.2.7)$$

Ferromagnetism and antiferromagnetism are ordered states of magnetism which only exist below a critical (Néel) temperature T_c . Above this temperature thermal vibrations oppose the ordering of the system typically leading to the material becoming paramagnetic. These

ordered phases of magnetism are of great interest in recent research, particularly in fields such as spintronics where ferromagnetic materials are regularly used to build devices based on the nature of electron spin rather than charge. Antiferromagnets are also of interest in the field of spintronics[13] and since the nature of these devices relies on the direction of spin of electrons passing through the materials, surface effects which may differ from those in the bulk could have an impact on behaviour at interfaces etc. The aim of this report is to establish the nature of surface effects in ferromagnetic and antiferromagnetic materials and to study their qualitative behaviour.

Examples of the kind of spontaneous symmetry breaking observed in these ordered magnetic materials occur in many areas of physics, such as changes of phase between solid and liquid or the change of behaviour of superconducting materials. Phase changes are therefore a well established area of study in thermodynamics and there is a system of classification of phase changes, which establishes the order of phase change based upon which order of derivative of a state variable of the system becomes discontinuous. Since the magnetic phase change of interest is of second order it is possible to apply Ginzburg-Landau theory to analyze the behaviour of the system near the critical temperature.

1.3 Ginzburg-Landau theory of second order phase transitions

Landau's theory of second order phase transitions is a very important method for studying systems which exhibit phase changes. Many of the effects and theories discussed later make extensive use of the theory and as such a brief introduction to the method is included here.

Landau theory is concerned with writing down a Landau functional L which depends on an order parameter η of the system, and coupling constants K_i . There are several further constraints placed on the form of L ,

- L must be consistent with all of the symmetries of the system.
- The order parameter should be any state variable of the system which is zero in the disordered phase but non-negative in the ordered phase. The order parameter should also be small near the critical temperature so that L can be approximated by a Taylor expansion in η .
- L should be minimised by $\eta = 0$ for $T > T_c$ and by $\eta \neq 0$ for $T < T_c$
- L should be analytic in η near the critical temperature allowing L to be expanded in a power series of η . In a homogeneous system this allows the **Landau free energy density** \mathcal{L} to be expressed as

$$\mathcal{L} = \frac{L}{V} = \sum_{n=0}^{\infty} a_n(K)\eta^n \quad (1.3.1)$$

- Should the system be inhomogeneous with an order parameter $\eta(r)$, \mathcal{L} is a local function, depending only upon $\eta(r)$ and a finite number of derivatives.

From these assumptions it is now possible to explicitly formulate the Landau free energy density. Since η is expected to be small we assume that terms beyond the fourth order can be neglected, the expansion is therefore [14].

$$\mathcal{L} = a_0 + a_1\eta + a_2\eta^2 + a_3\eta^3 + a_4\eta^4. \quad (1.3.2)$$

Minimising with respect to η gives.

$$\frac{\partial \mathcal{L}}{\partial \eta} = a_1 + 2a_2\eta + 3a_3\eta^2 + 4a_4\eta^3 = 0. \quad (1.3.3)$$

Now for $T > T_c$ we have $\eta = 0$, therefore it follows that $a_1 = 0$. Due to the symmetries of the system concerned, such as symmetry under time inversion, we require that L is an even function, i.e. $\mathcal{L}(\eta) = \mathcal{L}(-\eta)$ and this means that all coefficients of odd powers of η must also be equal to 0.

For $T < T_c$, since L should be minimised for $\eta > 0$ it is necessary to require $a_4 > 0$ otherwise a minimum could be approached by $\eta \rightarrow \infty$ and we are concerned with behaviour where η is positive, finite and small in the vicinity of T_c .

For $T = T_c$, a_2 should be equal to zero, this is because for temperatures above T_c the Landau free energy should be minimised by $\eta = 0$, requiring $a_2 > 0$ while for temperatures below T_c it should be minimised by $\eta \neq 0$ requiring $a_2 < 0$.

Taking all of the above into consideration we arrive at

$$\mathcal{L} = A(K, T)\eta^2 + B(K, T)\eta^4, \quad (1.3.4)$$

where $A(K, T)$ and $B(K, T)$ are coefficients which depend upon the temperature and coupling constants of the system. Since the ordered phase of the system is the lower temperature phase then after expanding A around T_c .

$$A(K, T) = a(K)(T - T_c).$$

It follows that a will be positive. We can therefore set the coefficient $B(K, T) = b(K) > 0$. Now L has the following form.

$$\mathcal{L} = a(K)(T - T_c)\eta^2 + b(k)\eta^4. \quad (1.3.5)$$

Now to check the behaviour of the function we differentiate with respect to η and minimise.

$$\frac{\partial \mathcal{L}}{\partial \eta} = 0 \quad \Rightarrow \quad \eta(A + 2b\eta^2) = 0.$$

Solving for η leads to:

$$\eta = 0 \quad \text{or} \quad \eta = \pm \sqrt{\frac{-a}{2b}(T - T_c)}.$$

Now that the positions of the extrema have been established, differentiating a second time will yield their classifications.

$$\left(\frac{\partial^2 \mathcal{L}}{\partial \eta^2}\right)_{\eta=0} = 2a(T - T_c), \quad \left(\frac{\partial^2 \mathcal{L}}{\partial \eta^2}\right)_{\eta=\pm\sqrt{\frac{-a}{2b}(T-T_c)}} = -4a(T - T_c). \quad (1.3.6)$$

Since we wish to find the minima of the function we require that the second derivatives in (1.3.6) are positive. This leads to the conclusion that the energy density is minimised for $T > T_c$ with $\eta = 0$ and for $T < T_c$ with $\eta = \pm\sqrt{\frac{-a}{2b}(T - T_c)}$. These conditions are consistent with the requirements stated earlier and allow the Landau free energy density to be used as a state variable in a similar way to the Gibbs free energy to calculate other values such as the magnetization of the system, by differentiating.

2 Surface Effects Induced by a Surface Boundary Condition

2.1 2-Lattice Antiferromagnetic Model

It is possible to theoretically show the existence of distinct surface effects in antiferromagnetic materials using a quasi-classical adaptation of the Heisenberg model shown in (1.2.7)

by introducing a surface boundary condition. This method was adopted by Mills[10]. In that investigation an fcc antiferromagnetic lattice was studied by treating the total lattice as an intersection of two ferromagnetic sublattices. Using this model each site from a given sublattice will have nearest neighbours, all of which belong to the other sublattice. It is therefore possible to write an expression for the average magnetization of a site in one sublattice as a function depending only on interactions with the other sublattice as shown.

$$\langle S_z^A(\vec{l}) \rangle = SB_s \left(\frac{g\mu_B H(\vec{l})}{k_B T} - \frac{J}{K_B T} \sum_{\vec{\delta}} \langle S_z^B(\vec{l} + \vec{\delta}) \rangle \right). \quad (2.1.1)$$

This equation is valid under the assumption that the site \vec{l} lies well within the bulk of the crystal where boundary conditions are negligible. In equation (2.1.1) $g\mu_B$ is the Landé g factor multiplied by the Bohr magneton, k_B is the Boltzmann constant, T is the absolute temperature of the system, S is the spin of the magnetic ions, with subscripts denoting components of spin and superscripts used to show belonging to either sublattice A or B, the sum over $\vec{\delta}$ is a summation over the 6 B sites which are the nearest neighbours of the A spin. Finally the function $B_s(x)$ is Brillouin function defined as follows.

$$B_s(x) = \left(1 + \frac{1}{2S} \right) \coth \left(S + \frac{1}{2} \right) x - \frac{1}{2S} \coth \left(\frac{x}{2} \right), \quad (2.1.2)$$

$$B_s(x) = \frac{1}{3}(s+1) \left\{ x - \frac{1}{15} [S(S+1) + \frac{1}{2}] x^3 + \dots \right\}. \quad (2.1.3)$$

In order to use Landau theory to study this model it is useful to introduce two quantities which simplify the dimensionality of the model. These quantities are the reduced temperature

$$\tau = T/T_N,$$

where T_N is the Néel temperature which for this model is $T_N = 2Js(S+1)$ and the dimensionless quantity

$$h(\vec{l}) = \left(\frac{g\mu_B}{k_B T_N} \right) H_A(\vec{l}).$$

Now defining the order parameters as follows

$$\eta_{A,B}(\vec{l}) = \langle S_{\vec{l},B}^z(\vec{l}) \rangle / S,$$

equation (2.1.1) may then be rewritten as

$$\eta_A(\vec{l}) = B_S \left(\frac{h(\vec{l})}{\tau} - \frac{1}{2\tau(S+1)} \sum_{\vec{\delta}} \eta_B(\vec{l} + \vec{\delta}) \right). \quad (2.1.4)$$

The assumption is made that $h_A(\vec{l})$ induces effects which vary slowly in space on the scale of the lattice constant. This enables us to regard $\eta_B(\vec{l})$ as a continuous function of \vec{l} and write

$$\sum_{\vec{\delta}} \eta_B(\vec{l} + \vec{\delta}) \cong 6\eta_B(\vec{l}) + a_0^2 \nabla^2 \eta_B(\vec{l}), \quad (2.1.5)$$

(2.1.4) now becomes

$$\eta_A(\vec{l}) = B_S \left(\frac{h(\vec{l})}{\tau} - \frac{3}{\tau(S+1)} \eta_B(\vec{l}) - \frac{3a_0^2}{\tau(S+1)} \nabla^2 \eta_B(\vec{l}) \right). \quad (2.1.6)$$

Now by applying the expansion in (2.1.3) to the Brillouin function in (2.1.6) using the assumption that the order parameter $\eta_{A,B}$ is small and retaining only the first order terms in $h_A(\vec{l})$ and $\nabla^2\eta_B$ one obtains a Ginzburg-Landau equation of the following form

$$\frac{1}{6}a_0^2\nabla^2\eta_B(\vec{x}) + \frac{1}{\tau}\eta_B(\vec{x}) + \eta_A(\vec{x}) - \beta\eta_B^3(\vec{x}) = \frac{(S+1)}{3\tau}h(\vec{x}). \quad (2.1.7a)$$

In (2.1.7a) $\beta = \frac{3}{5}[S(S+1) + \frac{1}{2}]/(S+1)^2$ is introduced as a dimensionless quantity with a constant value approximately equal to one.

If instead of a spin on the A lattice we consider a spin on the B lattice we find a further similar equation linking $\eta_{A,B}(\vec{x})$ to the externally applied field.

$$\frac{1}{6}a_0^2\nabla^2\eta_A(\vec{x}) + \frac{1}{\tau}\eta_A(\vec{x}) + \eta_B(\vec{x}) - \beta\eta_A^3(\vec{x}) = \frac{(S+1)}{3\tau}h(\vec{x}). \quad (2.1.7b)$$

2.2 Introducing a Surface Boundary Condition

We will now attempt to apply equations (2.1.7) to a semi-infinite crystal. In order to do this we must impose a boundary condition at the surface. In this example we take the crystal surface to lie in the x-y plane with the crystal occupying the region from $z = 0$ to $z = \infty$. It is now necessary to find appropriate boundary conditions for the functions η_A and η_B at the crystal surface, i.e. for $z = 0$.

To construct the boundary conditions we consider that the exchange integral varies near the surface of the crystal due to the lowering of localised reflectional symmetry, this variance will contribute to a change in the energy states of the system near the boundary. If $J(\vec{\delta})$ is the exchange interaction seen between a given site on the A lattice and it's neighbour on the B lattice separated by a distance $\vec{\delta}$ one can show that

$$\sum_{\vec{\delta}} \frac{J(\vec{\delta})}{J} \eta_B(\vec{l} + \vec{\delta}) = \left(5\eta_B - 4\Delta\eta_B + a_0 \frac{\partial\eta_B}{\partial z} + (1 - \Delta)a_0^2\nabla_{\parallel}^2\eta_B + \frac{a_0^2}{z} \frac{\partial^2\eta_B}{\partial z^2} \right)_{z=0}, \quad (2.2.1)$$

where $\Delta = \Delta J/J$ is the ratio of the variation in exchange interaction caused by the introduction of the surface and the exchange interaction within the bulk of the material. Also $\nabla_{\parallel}^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2$. It is now possible to notice from the forms of (2.1.5) and (2.2.1) that it is possible to apply Ginzburg-Landau equations throughout the entire crystal, including the surface layers. This requires the imposition of the boundary condition

$$(1 + 4\Delta)\eta_B + a_0^2\Delta\nabla_{\parallel}^2\eta_B + \frac{a_0^2}{6} \frac{\partial^2\eta_B}{\partial z^2} \Big|_{z=0} = a_0 \frac{\partial\eta_B}{\partial z} \Big|_{z=0}. \quad (2.2.2)$$

Since equations (2.1.7) are only applicable for values of the order parameter which vary slowly over the scale of lattice constant we will neglect spatial derivatives on the left hand side of (2.2.2) of higher than first order. This gives

$$(1 + 4\Delta)\eta_B|_{z=0} = a_0 \frac{\partial\eta_B}{\partial z} \Big|_{z=0}. \quad (2.2.3a)$$

For a field experienced by a spin in the B lattice near the surface. Similarly a boundary condition of the same form is obtained for a spin belonging to the A lattice,

$$(1 + 4\Delta)\eta_A|_{z=0} = a_0 \frac{\partial\eta_A}{\partial z} \Big|_{z=0}. \quad (2.2.3b)$$

2.3 Emergence of Surface Effects Due To Boundary Condition

Now that an appropriate boundary condition has been obtained for the surface region of the crystal it is possible to use Ginzburg-Landau equations to determine the spatial and temperature dependence of the ordering of the crystal near the Néel temperature.

For a case where $T < T_N$ ($\tau < 1$) and in the absence of an applied magnetic field, equations (2.1.7) with boundary conditions (2.2.3) accept a solution with

$$\eta_A(\vec{x}) = -\eta_B(\vec{x}) = \eta(\vec{x}).$$

This solution describes a state below the critical temperature exhibiting antiferromagnetic order. The function of $\eta(\vec{x})$ satisfies the homogeneous nonlinear equation

$$\frac{1}{6}a_0^2\nabla^2\eta(\vec{x}) + \left(\frac{1}{\tau-1}\right)\eta(\vec{x}) - \beta\eta^3(\vec{x}) = 0 \quad (2.3.1)$$

along with the boundary condition at $z = 0$

$$\eta = \frac{a_0}{1+4\Delta} \frac{\partial\eta}{\partial z}. \quad (2.3.2)$$

For temperatures near the Néel temperature and in the absence of an external field we find that $\eta(\vec{x})$ depends only on z so that (2.3.1) becomes

$$\frac{a_0}{6} \frac{\partial^2\eta}{\partial z^2} + (1-\tau)\eta(z) - \beta\eta^3(z) = 0. \quad (2.3.3)$$

It is expected that in the bulk of the crystal, i.e. far away from the surface, that η will be independent of z . It is therefore equal to the value η_∞ which can be deduced from equation (2.3.3) taking η to be independent of z to give

$$\eta_\infty = (1-\tau)^{\frac{1}{2}}/\beta^{\frac{1}{2}}. \quad (2.3.4)$$

It is predicted by molecular field theory that the order parameter vanishes as $(T_N - T)^{\frac{1}{2}}$ as T approaches T_N from below.

If we now express $\eta(z)$ as follows

$$\eta(z) = \eta_\infty f(z) \quad (2.3.5)$$

and measure distance in terms of the correlation length $\xi = a_0/[6(1-\tau)]^{\frac{1}{2}}$ by writing $z = \xi y$. equations (2.3.2) and (2.3.3) become

$$\frac{\partial^2 f}{\partial y^2} + f(y) - f^3(y) = 0, \quad (2.3.6)$$

where at $y = 0$,

$$f = \frac{a_0}{(1+4\Delta)\xi} \frac{\partial f}{\partial y}. \quad (2.3.7)$$

It is not possible to obtain an exact solution to equation (2.3.6) with the boundary conditions $f(y) \rightarrow 1$ as $y \rightarrow \infty$ and the $y = 0$ boundary condition given in (2.3.7). It is however possible to obtain an approximate solution which is valid near the critical temperature. Near the critical temperature $\xi \gg a_0$, so since it is expected that $\frac{\partial f}{\partial y}$ is of the order of unity then

$$f(0) = \frac{a_0}{(1+4\Delta)\xi} \frac{\partial f}{\partial y} = \text{order of } \frac{a_0}{\xi} \ll 1. \quad (2.3.8)$$

The function $f(0)$ will therefore be very small at $y = 0$ when T is near T_N . If we now introduce a function $f^{(0)}(y)$ that satisfies equation (2.3.6) subject to the boundary conditions

$$f^{(0)}(0) = 1, \quad f^{(0)}(\infty) = 1. \quad (2.3.9)$$

The exact solution of equation (2.3.6) with boundary conditions from (2.3.7) may now be written as

$$f(y) = f^{(0)}(y) + f^{(1)}(y), \quad (2.3.10)$$

where for T near T_N , $f^{(1)}(y)$ is small compared with $f^{(0)}(y)$. When $f^{(1)} \ll f^{(0)}$, it is possible to obtain $f^{(1)}$ from the differential equation

$$\frac{\partial^2 f^{(1)}}{\partial y^2} + (1 - 3f^{(0)2})f^{(1)} = 0 \quad (2.3.11)$$

where

$$f^{(1)}(0) = \frac{a_0}{(1 + 4\Delta)\xi} \frac{\partial f^{(0)}(0)}{\partial y}, \quad f^{(1)}(\infty) = 0. \quad (2.3.12)$$

If we now limit our interest to the surface layer we can see that $f(0) = f^{(0)}(0) + f^{(1)}(0) \equiv f^{(1)}(0)$. Therefore if $f^{(0)}(y)$ is known it is possible to find the order parameter with no need to solve equation (2.3.11). It may be shown that

$$f^{(0)}(y) = \tanh(y/\sqrt{2}). \quad (2.3.13)$$

It therefore follows that

$$f^{(1)}(0) = \frac{a_0}{\sqrt{2}(1 + 4\Delta)\xi} = \frac{\sqrt{3}}{(1 + 4\Delta)} \left(\frac{T_N - T}{T_N} \right)^{1/2}. \quad (2.3.14)$$

It is now possible to express the sublattice magnetization $\langle S_z \rangle|_{\text{surf}}$ in the surface as

$$\langle S_z \rangle|_{\text{surf}} = S\eta(0) = S\eta_\infty f^{(1)}(0)$$

or

$$\langle S_z \rangle|_{\text{surf}} = \frac{\sqrt{3}S}{\sqrt{\beta}(1 + 4\Delta)} \left(\frac{T_N - T}{T_N} \right). \quad (2.3.15)$$

In molecular field theory, near the Néel temperature the temperature dependence of $\langle S_z \rangle|_{\text{surf}}$ is proportional to $T_N - T$. From equation (2.3.15) we can see that the surface magnetization $\langle S_z \rangle|_{\text{surf}}$ near the Néel temperature depends on the value of Δ . If the exchange constants are softened, i.e. $\Delta > 0$ then the magnitude of the surface magnetization is decreased but the temperature dependence is unaffected. If however the exchange integral is stiffened ($\Delta < 0$) then for $|\Delta| > \frac{1}{4}$, $\langle S_z \rangle|_{\text{surf}}$ becomes negative. From molecular field theory it is predicted that the surface will order antiferromagnetically at a temperature above the Néel temperature of the bulk. Since this effect is confined to only a few layers in the surface region and it is known that true antiferromagnetic order cannot be realised in two-dimensions, it is unlikely that this magnetic ordering of surface regions above the Néel temperature of the bulk would take place in a real crystal. It is likely that this effect is a remnant of the molecular field theory from which it is derived, it is interesting to note however that this theoretical result does predict that for a surface exchange appreciably larger than that in the bulk, at temperatures far above T_N there may be long range correlations between spins in the surface region where correlations between bulk spins remain of the order a_0 .

3 Dzyaloshinsky-Moriya Exchange Interactions

The Heisenberg model described above takes into account a simple form of interaction between neighbouring particles as denoted by the exchange constant J . However it was noticed that in certain antiferromagnetic crystals, a "weak" net magnetic moment was observed experimentally, despite the crystal being in the antiferromagnetic regime. It was initially proposed that this moment may be present due to the formation of antiferromagnetic domains with magnetized walls. It was noted however, that this situation is energetically unfavourable and is only likely to exist in the vicinity of crystal impurities. Experiments undertaken with very pure samples found that the magnitude of the net magnetic moment was unaffected by sample purity, and was present even in very pure sample crystals.

3.1 Symmetry Argument for Existence of "Weak" Ferromagnetism

Despite the non dependence of the spontaneous moment on the purity of the crystal, dependence on the symmetry of the structure was apparent. In order to attempt to explain the presence of the ferromagnetic moment in the antiferromagnetic crystal, Dzyaloshinsky [6] proposed a solution based on symmetry arguments. If it is possible to construct a spin arrangement which is invariant under all transformations of the space group of the magnetic lattice, where the net magnetization within the unit cell is non-zero, then there may be another mechanism responsible for the ferromagnetism than the one proposed above. Such an arrangement would allow for the existence of such a moment without the need for crystal impurities.

In order to try and construct such a scenario a rhombohedral lattice example is used, in particular the isomorphous crystals α -Fe₂O₃ and Cr₂O₃. This unit cell consists of four magnetic ions with spins arranged such that the net magnetic moment of the unit cell is zero. The four ions lie along the space diagonal of the rhombohedron. The direction of the spins has not been determined for Cr₂O₃ but for α -Fe₂O₃ the orientations depend on temperature. Two antiferromagnetic states are observed in α -Fe₂O₃, at $T < 250K$ the spins are along the crystal axis (state 1), and at $250K < T < 950K$ the spins lie in one of the vertical axes of symmetry. Neutron diffraction studies of these two crystals have shown that the magnetic unit cell is identical to the space unit cell with the spins of the four ions differing in sign only and the sum of spins in a cell being equal to zero. The spin arrangements are $s_1 = -s_2 = -s_3 = s_4$ for α -Fe₂O₃ and $s_1 = -s_2 = s_3 = -s_4$ in Cr₂O₃. From experimental measurement it appears that Cr₂O₃ is not ferromagnetic at all while α -Fe₂O₃ is ferromagnetic in state 2.

If we now assume that the symmetry of the antiferromagnetic distribution is known, we can consider the question of whether it is possible, within this symmetry, to construct an arrangement where the sum of the spins within the unit cell is non zero. One possibility to consider is the situation where the four spins rotate out of their symmetry plane towards one another. The question is now to determine whether the symmetry of this distribution is identical to the symmetry of the arrangement in state 2.

When determining the symmetry properties of a magnetic crystal it is not merely the distribution of the atoms within the unit cell which must be considered. It is also necessary to consider the average spin $s(x, y, z)$ at every point. This vector quantity may be invariant under a number of spatial transformations but it is also possible that an extra symmetry element R may exist which consists of a reversal of the spin sign $s(x, y, z) \rightarrow -s(x, y, z)$. This operation arises from the invariance of the equations of mechanics with respect to the changing of the sign of time and of the sign of magnetic

fields and spins simultaneously. For a spin distribution to be invariant under R by itself we must have $s(x, y, z) = -s(x, y, z) = 0$ and the crystal will be in the paramagnetic phase. It is possible though for an arrangement with non zero $s(x, y, z)$ to have invariance with respect to R when it is combined with other symmetry operations. The "magnetic" space group is therefore not entirely identical to the space symmetry group.

The aim is now to determine the class of symmetry in each antiferromagnetic state. As well as the two possible antiferromagnetic states mentioned above it is also worth noting for considerations of symmetry a third state with the spins aligned along one of the second order axes. It is now possible, using the description of the space group of the lattice to find the classes to which the three states belong and to write down the elements of symmetry which relate to each state [7].

$$C_3, U_2, I, S_6, \sigma_d \quad (\text{State 1})$$

$$U_2, I, \sigma_d \quad (\text{State 2})$$

$$U_2R, I, \sigma_dR. \quad (\text{State 3})$$

Now that the elements of symmetry for each state have been identified we can now consider whether a magnetic moment can exist in any of the states which is invariant under all of the symmetry transformations in the class. We can see that state one cannot possess a net magnetic moment as the symmetry group contains a third-order axis with a second-order one perpendicular to it. It is therefore not possible to choose a direction for a magnetic moment which would allow it to be invariant under the necessary transformations. For the cases of states 2 and 3 however, it is possible to choose a direction for a non zero net magnetic moment. For case 2 the moment lies along the second order axis and in state 3 it lies in a plane of symmetry.

We can therefore see that the experimental observation that $\alpha\text{-Fe}_2\text{O}_3$ does not possess a ferromagnetic moment in the state 1 arrangement follows directly from the magnetic symmetry of the crystal structure. We can also see why a moment is observed experimentally in the state 2 and show that it must be directed along one of the second order axes, perpendicular to the plane of symmetry in which the antiferromagnetic components of the spins lie.

As shown above it is therefore allowable within the symmetry of the crystal for a ferromagnetic moment to occur. The symmetry does not however, limit the magnitude of this moment, it is permissible without breaking symmetry for the spins within the cell to rotate so as to coincide creating a purely ferromagnetic material. In order to investigate the weak nature of the experimentally observed net magnetic moment we will now apply Ginzburg-Landau theory.

3.2 Ginzburg-Landau Analysis

In order to describe the state of a magnetic crystal we define the average density of the spin distribution as $s(x, y, z)$. Where there is more than one magnetic ion present within each unit cell the state of each ion is described by its own spin density function $s_i(x, y, z)$. Since the spin function $s(x, y, z)$ describes the crystals magnetic state it must possess the same symmetry properties as the magnetic crystal. The phase transitions being investigated are of the second kind and as such the spin density function $s(x, y, z)$ (and therefore the magnitude and direction of the spins within the crystal) varies continuously while its symmetry changes suddenly. This also means that at the point of transition between phases, the symmetries of both are identical.

The specific transition we are concerned with is between the paramagnetic and the antiferromagnetic phases. In the paramagnetic phase $s(x, y, z) = 0$ and the symmetry

group is described by one of the 230 which contain the operation R by itself. In the antiferromagnetic phase $s(x, y, z) \neq 0$, although since the phase is antiferromagnetic the integral of the spin density over the entire unit cell $\int sdV = 0$ and the crystal's magnetic symmetry is the same as the symmetry of the function $s(x, y, z)$.

From group theory it is known that any basis function can be represented by a linear combination of functions which transform one into the other under all transformations of the group since the resulting representation while different, differs only by a similarity transform from the one representing the original basis function. If we therefore let $\phi_1(x, y, z), \phi_2(x, y, z) \dots$ be functions which transform one into another under all transformations of the symmetry group of the paramagnetic phase it is possible to represent the spin density function in the antiferromagnetic phase as a linear combination of these functions

$$s_\alpha(x, y, z) = \sum_i a_{\alpha i} c_i \phi_i(x, y, z), \quad (3.2.1)$$

where we have chosen the coefficients $a_{\alpha i}$ to be temperature and pressure independent in such a way as to allow $s_\alpha(x, y, z)$ to transform as pseudovector components.

As mentioned above it is possible to replace the functions ϕ_i by any linear combination of them. It is also always possible to select ϕ_i in such a way as to be able to form a series of sets, each containing the minimum number of functions which transform one set into another under all symmetry operations of the symmetry group. Each of these minimal sets of functions is then an irreducible representation of the symmetry group and the expansion of $s(x, y, z)$ can be rewritten as

$$s_\alpha(x, y, z) = \sum_n \sum_i a_{\alpha i}^{(n)} c_i^{(n)} \phi_i^{(n)}(x, y, z), \quad (3.2.2)$$

where n denotes the number of an irreducible representation and i is the number of a function in it's base.

Since in the paramagnetic phase the crystal symmetry group contains R by itself we now consider the behaviour of the irreducible representations under the action of R . It is possible to split them into two types, those which reverse their sign under the action of R and those which are invariant. Since the spin density function $s(x, y, z)$ itself changes sign under the action of R the expansion given by (3.2.2) will contain only those functions who also change their sign under the action of R .

If we now consider the thermodynamic potential Φ of the crystal with spin density $s(x, y, z)$, this depends on temperature, pressure and the coefficients $c_i^{(n)}$. The dependence of the coefficients $c_i^{(n)}$ on temperature, pressure and the symmetry of the crystal in the antiferromagnetic phase can be determined through the minimization of Φ . Since $s(x, y, z) = 0$ in the paramagnetic phase, $c_i^{(n)}$ are zero in this phase. at the transition point the coefficients will become zero and below but near the critical temperature they will have a small non-negative value. This suggests that we can expand Φ as a power series of $c_i^{(n)}$.

When we previously expanded $s(x, y, z)$ we considered $c_i^{(n)}$ to be constants and $\phi_i^{(n)}(x, y, z)$ to be functions which were changeable under the transformations of the group. It is equally valid to consider $\phi_i^{(n)}$ to be constant and allow $c_i^{(n)}$ to vary under the group transformations. Since Φ is invariant under all symmetry operations of the group then to expand it as a power series of $c_i^{(n)}$ the expansion must contain only terms which are also invariant. Since all of the coefficients $c_i^{(n)}$ change their sign under the action of R the expansion must therefore only contain terms which are even powers of $c_i^{(n)}$ and which are therefore invariant under such a transformation. From group theory we know that there is only one way

to construct an invariant from quantities transforming under an irreducible representation and that it is a definite quadratic form always expressible as a sum of squares. We can therefore see that the expansion of Φ will be of the form

$$\Phi = \Phi_0 + \sum_n A^{(n)} \sum_i c_i^{(n)2}, \quad (3.2.3)$$

where here, Φ_0 is the potential of the paramagnetic phase, and $A^{(n)}$ are functions of P and T .

If we now consider the paramagnetic phase, when Φ is a minimum, $c_i^{(n)} = 0$, this means that all of the functions $A^{(n)} > 0$. The phase transition to antiferromagnetism therefore takes place when one of the functions $A^{(n)}$ becomes negative. At the point of transition $A^{(n)} = 0$. This leads to the constant $c_i^{(n)}$ of the corresponding irreducible representation becoming non-zero. The symmetry of the crystal now changes into the antiferromagnetic regime and is the same as the symmetry of the spin density function

$$s_\alpha(x, y, z) = \sum_i a_{\alpha i}^{(n)} c_i^{(n)} \phi_i^{(n)}(x, y, z). \quad (3.2.4)$$

In order to find the actual form of the symmetry it is necessary to take into account the fourth order terms in $c_i^{(n)}$. If we introduce the order parameter η as follows (from now on the index n will be omitted for brevity).

$$\eta^2 = \sum_i c_i^2, \quad c_i = \gamma_i \eta, \quad (3.2.5)$$

we can now rewrite our previous expansion of Φ as

$$\Phi = \Phi_0(P, T) + \eta^2 A(P, T) + \eta^4 \sum_k B_k(P, T) f_k^4(\gamma_i) \quad (3.2.6)$$

where the functions f_k^4 are invariants of the fourth order which can be made up from γ_i .

It is now possible to find γ_i from the minimum condition of Φ , allowing us to rewrite Φ in the more usual form used in Landau theory similar to the form shown in (1.3.4)

$$\Phi = \Phi_0(P, T) + \eta^2 A(P, T) + \eta^4 B(P, T) \quad (3.2.7)$$

and in the usual way determine the dependence of the order parameter η on P and T .

Calculation of η^2 and γ_i in this manner can then be used to determine the symmetry of the average spin density function s_α and therefore the symmetry of the crystal in the antiferromagnetic phase.

We next note that the change in magnetic phase of α -Fe₂O₃ takes place without any change of the unit cell. This allows us to consider the average spin density function $s(x, y, z)$ as being coordinate independent and therefore the symmetry of the crystal is governed simply by the average values of the spins of the four ions. It is now not necessary to distinguish between the coefficients $c_i^{(n)}$ and the functions $\phi_i^{(n)}$ in equation (3.2.2) and we can now regard their product $c_i^{(n)} \phi_i^{(n)}$ as a linear combination of the components of the four ions $\vec{s}_1, \vec{s}_2, \vec{s}_3, \vec{s}_4$. This linear combination must also transform according to the appropriate irreducible representation of the paramagnetic phase symmetry group. For the crystal being considered this group is $D_{3d}^6 \times R$ [7, p. 548-551].

Near the critical temperature the average spins of the ions will be small and the thermodynamic potential Φ can be expanded as a power series of their components. As was the case when expanding about $c_i^{(n)}$ we are only concerned with terms which are

invariant under the transformation R and therefore only even powered terms are retained. Φ must also be invariant under the operations of the crystal symmetry group. Since there is no change of the unit cell we regard any translation by a whole period as an identicle transformation. The space group D_{3d}^6 therefore becomes \tilde{D}_{3d}^6 which differs by the replacement of certain rotation axes and symmetry planes with helical axes and glide surfaces.

The axial vectors $\vec{s}_1, \vec{s}_2, \vec{s}_3, \vec{s}_4$ form a reducible representation of the \tilde{D}_{3d}^6 space group. In order to form an irreducible representation we introduce new basis vectors $\vec{m}, \vec{l}_1, \vec{l}_2, \vec{l}_3$ which are given by

$$\begin{aligned}\vec{m} &= \vec{s}_1 + \vec{s}_2 + \vec{s}_3 + \vec{s}_4 & \vec{s}_1 &= \frac{1}{4}(\vec{m} + \vec{l}_1 + \vec{l}_2 + \vec{l}_3) \\ \vec{l}_1 &= \vec{s}_1 - \vec{s}_2 - \vec{s}_3 + \vec{s}_4 & \vec{s}_2 &= \frac{1}{4}(\vec{m} - \vec{l}_1 - \vec{l}_2 + \vec{l}_3) \\ \vec{l}_2 &= \vec{s}_1 - \vec{s}_2 + \vec{s}_3 - \vec{s}_4 & \vec{s}_3 &= \frac{1}{4}(\vec{m} - \vec{l}_1 + \vec{l}_2 - \vec{l}_3) \\ \vec{l}_3 &= \vec{s}_1 + \vec{s}_2 - \vec{s}_3 - \vec{s}_4 & \vec{s}_4 &= \frac{1}{4}(\vec{m} + \vec{l}_1 - \vec{l}_2 - \vec{l}_3).\end{aligned}$$

The vector \vec{m} here simply represents the average magnetic moment of a unit cell.

The components of \vec{m} and \vec{l}_i transform independently under each of the symmetry transformations. These components transform according to unidimensional representations $A_{2g}, A_{1g}, A_{1u}, A_{2u}$ of the point group D_{3d} . The x and y components of the vectors \vec{m} and \vec{l}_1 transform according to the same two-dimensional representation E_g and these components of the vectors \vec{l}_2 and \vec{l}_3 according to E_u .

Now that we have established the irreducible representations according to which the components of the basis vectors transform we may construct the most general form of the expansion of Φ allowable by the symmetry of the system. Limiting the expansion to second order terms gives

$$\begin{aligned}\Phi &= \frac{A_1}{2}l_1^2 + \frac{A_2}{2}l_2^2 + \frac{A_3}{2}l_3^2 + \frac{B}{2}m^2 + \frac{\alpha_1}{2}l_{1z}^2 + \frac{\alpha_2}{2}l_{2z}^2 + \frac{\alpha_3}{2}l_{3z}^2 + \\ &+ \frac{b}{2}m_z^2 + \beta_1(l_{1x}m_y - l_{1y}m_x) + \beta_2(l_{2x}l_{3y} - l_{2y}l_{3x}).\end{aligned}\quad (3.2.8)$$

In the expansion (3.2.8) there are several magnetic energy terms which correspond to various types of spin interactions. The terms of the form Al^2 do not depend on the orientation of the \vec{l} vector or the spin orientations and represent exchange interactions such as those described by the Heisenberg model. Terms of the form αl_z^2 and $(l_x m_y - l_y m_x)$ are due to relativistic spin-lattice interactions and the magnetic dipole interaction and determine the magnetic anisotropy of the crystal.

The important feature of the thermodynamic potential of crystals with symmetries such as those discussed here is the presence of the mixed terms $l_{1x}m_y - l_{1y}m_x$ and $l_{2x}l_{3y} - l_{2y}l_{3x}$. From a purely mathematical point of view these terms are a result of the x and y components of \vec{m} and \vec{l}_1 (and also \vec{l}_2 and \vec{l}_3) transforming according to the same representations. The physical interpretation however, is that it is the first of these mixed terms which is responsible for the ferromagnetic moment in the crystal, and that this moment is a result of relativistic rather than exchange interactions.

3.3 Moriya's Microscopic picture of Anisotropic Superexchange Interaction

The Dzyaloshinsky picture described above is a purely phenomenological argument showing that the existence of a ferromagnetic moment is possible in an antiferromagnetic crystal structure. The nature of the interaction described in Dzyaloshinsky's phenomenological

picture shows that there is a term which favours a canted alignment of spins rather than an antiferromagnetic arrangement, which is necessary in establishing a ferromagnetic moment. The term responsible for this can be expressed as

$$\vec{D} \cdot (\vec{S}_1 \times \vec{S}_2), \quad (3.3.1)$$

where \vec{D} is a constant vector [11]. It can be seen that (3.3.1) is the antisymmetric part of the most general expression for a bilinear spin-spin interaction. These spin-spin interactions can be due to either isotropic superexchange interaction, magnetic dipole-dipole interaction or anisotropic superexchange interaction. It is the anisotropic superexchange interaction which was investigated by Moria in a quantitative manner in order to provide a method for calculating the vector \vec{D} , the approach involves the use of the formalism proposed by Anderson [1] for consideration of superexchange interactions. This involves treatment of the d-orbital electrons as single electron wavefunctions interacting with a field sufficiently modified to represent the lattice of ions. The Hamiltonian is then constructed and diagonalized accounting for the localization of the electrons to the cations of the lattice and the repulsive nature of the inter-electron interactions. The approach involves second-quantization and as such, the specifics of the mathematical techniques employed are beyond the scope of the present discussion, but the treatment leads to an expression for the \vec{D} vector of the form

$$\begin{aligned} \vec{D}_{RR'} = & - \left(\frac{i}{U^2} \right) \left\{ \sum_{m'} J_{n'm'}(R') \left[b_{nm'}(R - R') \times \vec{C}_{m'n}(R' - R) \right. \right. \\ & \left. \left. - \vec{C}_{nm'}(R - R') b_{m'n}(R' - R) \right] \right. \\ & + \sum_m J_{nm}(R) \left[b_{n'm}(R' - R) \vec{C}_{mn'}(R - R') \right. \\ & \left. \left. - \vec{C}_{n'm}(R' - R) b_{mn'}(R - R') \right] \right\}. \end{aligned}$$

Direct calculation of this coefficient is possible only in the simplest of configurations and the real insight gained is that the order of magnitude of \vec{D} can be estimated by $D \sim (\Delta g/g)J$. It is also simple to establish a set of conditions which will determine the direction of the \vec{D} vector depending on the crystal arrangement. If we consider a case where there are two ions located at the points A and B with a point bisecting the line AB denoted by C

- When C is a centre of inversion symmetry

$$\vec{D} = 0$$

- When a mirror plane perpendicular to AB passes through C

$$\vec{D} \parallel \text{mirror plane, or } \vec{D} \perp AB$$

- When there is a mirror plane including A and B

$$\vec{D} \perp \text{mirror plane}$$

- When a two-fold rotation axis perpendicular to AB passes through C

$$\vec{D} \perp \text{two-fold axis}$$

- When there is an n -fold axis ($n > 2$) along AB

$$\vec{D} \parallel AB$$

Symmetry again plays a large roll in determining the magnitude of the effect induced by these interactions. In crystals with high symmetry the coupling vanishes and it is only in low symmetry situations where it becomes of significance.

4 Dzyaloshinsky-Moriya Interactions Induced by the Introduction of a Surface

Since high local symmetry causes the antisymmetric interaction mentioned above to become negligible. Then in the presence of local disorder the effect is expected to have a noticeable influence on the magnetic structure. We will now consider a scenario where the bulk crystal has high enough symmetry to negate these interactions but where the introduction of a surface lowers local symmetry to a point where they become significant.

The interaction described in section 3 can be treated as an extra term in the interaction energy between two sites. This modifies the Heisenberg model shown in (1.2.7) to become

$$E = \sum_{i<j=1}^N J_{ij} \vec{S}_i \cdot \vec{S}_j + \sum_{i<j=1}^N \vec{D} \cdot (\vec{S}_i \times \vec{S}_j) + H \sum_{i=1}^N \vec{S}_i^z. \quad (4.0.2)$$

However, in the situations we will be looking at in this and future sections we will be assuming the absence of an external magnetic field leaving

$$E = \sum_{i<j=1}^N J_{ij} \vec{S}_i \cdot \vec{S}_j + \sum_{i<j=1}^N \vec{D} \cdot (\vec{S}_i \times \vec{S}_j). \quad (4.0.3)$$

Equation (4.0.3) will be the expression for the interaction energy used in the consideration of all of the situations which follow.

4.1 Dependence of \vec{D} vector on surface geometry

Since it is the local symmetry breaking induced by the addition of the surface which causes the D-M interaction to become significant it is also important to consider the orientation of the surface in order to ascertain the direction of the \vec{D} vector. We can apply the conditions described at the end of section 3.3 to establish the direction of the \vec{D} vector for a number of geometries. We will be limiting our consideration to nearest neighbour interactions since these are expected to have by far the greatest influence on the magnetic structure of the crystal. Next nearest neighbour interactions are not expected to have a significant impact on magnetic ordering.

Here we will consider several types of cubic crystal with three distinct surface planes. From Table 1 [4] it is clear to see that the direction of the \vec{D} vector is largely affected by the crystal geometry and is also influenced by the type of surface plane considered.

| | (0 0 1) surface | (1 0 1) surface | (1 1 1) surface |
|----------------------|---|--|--|
| Simple cubic lattice | (a) 1 neighbour in 1st layer $\vec{D}_1 = D\hat{z}$ | (d) 2 neighbours in 1st layer $\vec{D}_1 = D\hat{y}$ $\vec{D}_2 = -D\hat{y}$ | (g) 3 neighbours in 1st layer $\vec{D}_1 = -D\hat{x}$ $\vec{D}_2 = D(\frac{1}{2}\hat{x} - \frac{1}{2}\sqrt{3}\hat{y})$ $\vec{D}_3 = D(\frac{1}{2}\hat{x} + \frac{1}{2}\sqrt{3}\hat{y})$ |
| | (b) 4 neighbours in 1st layer $\vec{D}_1 = D(-\hat{x} + \hat{y})$ $\vec{D}_2 = D(-\hat{x} - \hat{y})$ $\vec{D}_3 = D(\hat{x} - \hat{y})$ $\vec{D}_4 = D(\hat{x} + \hat{y})$ | (e) 2 neighbours in 1st layer $\vec{D}_1 = -D\hat{x}$ $\vec{D}_2 = D\hat{x}$ | (h) 3 neighbours in 1st layer, 1 neighbour in 3rd layer $\vec{D}_1 = D(-\frac{1}{2}\hat{x} + \frac{1}{2}\sqrt{3}\hat{y})$ $\vec{D}_2 = D(-\frac{1}{2}\hat{x} - \frac{1}{2}\sqrt{3}\hat{y})$ $\vec{D}_3 = D\hat{x}$ $\vec{D}_4 = D'\hat{z}$ |
| FCC lattice | (c) 4 neighbours in the 1st layer $\vec{D}_1 = D\hat{y}$ $\vec{D}_2 = -D\hat{x}$ $\vec{D}_3 = -D\hat{y}$ $\vec{D}_4 = D\hat{x}$ | (f) 4 neighbours in the 1st layer, 1 neighbour in the 2nd layer $\vec{D}_1 = D(-\sqrt{\frac{2}{3}}\hat{x} + \sqrt{\frac{1}{3}}\hat{y})$ $\vec{D}_2 = D(-\sqrt{\frac{2}{3}}\hat{x} - \sqrt{\frac{1}{3}}\hat{y})$ $\vec{D}_3 = D(\sqrt{\frac{2}{3}}\hat{x} - \sqrt{\frac{1}{3}}\hat{y})$ $\vec{D}_4 = D(\sqrt{\frac{2}{3}}\hat{x} + \sqrt{\frac{1}{3}}\hat{y})$ $\vec{D}_5 = D'\hat{z}$ | (i) 3 neighbours in 1st layer $\vec{D}_1 = D(-\frac{1}{2}\hat{x} + \frac{1}{2}\sqrt{3}\hat{y})$ $\vec{D}_2 = D(-\frac{1}{2}\hat{x} - \frac{1}{2}\sqrt{3}\hat{y})$ $\vec{D}_3 = D\hat{x}$ |

Table 1: Direction of the \vec{D} vector for nearest neighbour sites at the surface and in the bulk for cubic crystal structures. The z axis is always normal to the surface plane while the x and y axes lie in the surface plane. D refers to the magnitude of the \vec{D} vector for sites in the 1st layer and D' to sites in the 2nd (or 3rd) layer below the surface

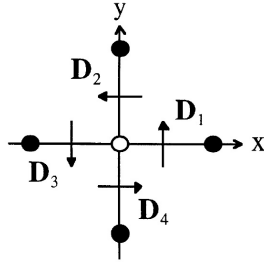


Figure 2: Direction of \vec{D} vector for arrangement (c) from table 1

4.2 Effect of Dzyaloshinsky Moriya Interaction on Magnetic Order Near the Surface of an Antiferromagnet

We have discussed the nature of the Dzyaloshinsky Moriya interaction and have used the symmetry rules postulated by Dzyaloshinsky to determine the direction of the \vec{D} vector coefficient at the surface boundary of several different crystal geometries and surface orientations. We now consider whether the inclusion of this effect will have any influence on the nature of the magnetic ordering near the surface boundary of an antiferromagnet.

If we consider the same geometry as in the Mills investigation discussed in section 2, then after treating the lattice as a system of 2 intersecting sublattices, we find that

the structure including the Dzyaloshinsky Moriya interactions will cause this model to be modified into a 4 sublattice model where each of the initial 2 sublattices is split into 2 further intersecting sublattices with a small canting between the spins of the order of D/J . This leads to the formation of a small ferromagnetic moment in the region close to the surface (within the first 1 or 2 atomic layers) with a direction normal to the surface plane. It is simple to see that this modification applies only in the antiferromagnetic phase. If the material is in a ferromagnetic state the the sum of the interactions leads to no net modification of the magnetic ordering and ferromagnetic order is maintained and unaltered.

If we further consider directions of the \vec{D} vectors for the individual interactions between a surface site and each of it's nearest neighbours in case (c) from Table 1 with axes as defined in figure 2 [4] we can see that the D-M interaction will tend to rotate the spins into a spiral magnetism state, i.e. chirality is induced into the system. This chirality will again be limited to a region which spans the first 2 or 3 atomic layers of the material from the surface. This induced chirality itself leads to the possibility of new effects arising within this region which will be discussed in the next section.

4.3 Effect of Induced Chirality in the Surface Region

The direction of the \vec{D} vector in case (c) will tend to cause the directions of the spins of the nearest neighbours to modify in such a way as to break chiral symmetry in the surface region [3].

Chiral symmetry breaking in crystals has been observed experimentally in several noncentrosymmetric ferromagnetic and antiferromagnetic compounds. For the purposes of our investigation into the chiral nature induced by the D-M interactions it is convenient to describe the antisymmetric exchange interaction term in the form of a Lifshitz invariant linear in first spacial derivatives of the magnetization $\vec{M}(\vec{r})$ of the form

$$\vec{M}_i \frac{\partial \vec{M}_j}{\partial x_l} - \vec{M}_j \frac{\partial \vec{M}_i}{\partial x_l}, \quad (4.3.1)$$

where x_l denotes a spatial coordinate.

These interactions cause a breaking in chiral symmetry and lead to the stabilization of localized vortices, with a fixed rotation sense of the magnetization. It is also possible to observe these effects in centrosymmetric crystals where stresses or applied magnetic fields may be used to induce chiral magnetic couplings. These effects, since they are largely due to the D-M interaction energy are expected to be negligible in the bulk, however they are expected to potentially play a role in the behaviour of magnetic thin films or near the surface of a larger crystal where local symmetry is sufficiently low as discussed in the previous section.

From experimental data collected regarding ferromagnetic layer systems, it can be seen that the magnetic properties of nanomagnets are substantially influenced by inhomogeneous stresses. We therefore assume that the chiral couplings should also be inhomogeneous within a magnetic structure where local symmetry is low. This allows us to write a phenomenological expression for the chiral energy density as

$$w_D = D\eta(\vec{r})L(\vec{m}), \quad (4.3.2)$$

where D is a constant, L is a Lifshitz invariant with the form given in (4.3.1) and the function $\eta(\vec{r})$ is a distribution function describing the inhomogeneous distribution of the magnetic chiral energy. This function $\eta(\vec{r})$ can be treated as field present in the crystal in addition to the magnetization field. This function then takes on the role of the chiral

order parameter and by application of Ginzburg-Landau theory it is possible to express the coupling energy as

$$w_c = \sum_i \tilde{A} \left(\frac{\partial \eta}{\partial x_i} \right)^2 + f(\eta^2) + D\eta(\vec{r})L(\vec{m}). \quad (4.3.3)$$

It is now our aim to find a form of $\eta(\vec{r})$ and of the Lifshitz invariant $L(\vec{m})$ which will minimise this chiral coupling energy. In order to do this we will consider the following geometry, a semi-infinite crystal which has a surface in the $z = 0$ plane and which occupies the region $z \leq 0$. We will assume that the function $\eta(\vec{r})$ is homogeneous along the surface and varies only with z , i.e. $\eta(\vec{r}) \rightarrow \eta(z)$. Equation (4.3.3) then becomes

$$w_c = \tilde{A} \left(\frac{\partial \eta}{\partial z} \right)^2 + f(\eta^2) + D\eta(z)L(\vec{m}). \quad (4.3.4)$$

Next we assume that the homogeneous energy function $f(\eta^2)$ can be expressed in a form similar to that of the Landau free energy given in equation (1.3.4)

$$f(\eta^2) = \frac{\alpha}{2}\eta^2 + \frac{b}{2}\eta^4$$

and take a Lifshitz coupling function as follows

$$L(\vec{M}) = m_z \frac{\partial m_x}{\partial x} - m_x \frac{\partial m_z}{\partial x} + m_z \frac{\partial m_y}{\partial y} - m_y \frac{\partial m_z}{\partial y}. \quad (4.3.5)$$

We now have sufficient knowledge of the form of w_c to attempt to minimize with respect to $\eta(z)$. Minimization with respect to \vec{M} requires a more in depth mathematical treatment involving the coupling of the chiral energy with the magnetic energy, which will not be discussed in this report. We will however consider the minimization with respect to η neglecting the magnetic energy, since this will have no dependence on η and can be done self consistently by minimization of w_c .

Minimizing with respect to $\eta(z)$ requires that we impose boundary conditions on the problem. If we assume some form of normalization such that at the surface (where chiral effects are expected to be a maximum) $\eta(z)$ has a maximal value and that the function decreases rapidly with z (since chiral effects are not expected to propagate any significant distance into the bulk) we can formulate the boundary conditions

$$\begin{aligned} \eta(z)_{(z=0)} &= 1, \\ \eta(z)_{(z=-\infty)} &= 0. \end{aligned}$$

Now minimizing (4.3.4) with respect to $\eta(z)$ gives

$$\tilde{A}\eta'^2 + \frac{\alpha}{2}\eta^2 + \frac{b}{4}\eta^4 = \text{constant}, \quad (4.3.6)$$

where $\eta' = \frac{d\eta}{dz}$.

We can now consider the boundary condition for $z = -\infty$ to establish the value of the constant in equation (4.3.6). Since we expect η to decrease to near zero within a relatively short distance of the surface we assume that $\eta' = 0$ at $z = -\infty$ which along with our initial boundary conditions leads to the conclusion that the constant in (4.3.6) is equal to zero.

$$\tilde{A}\eta'^2 + \frac{\alpha}{2}\eta^2 + \frac{b}{4}\eta^4 = 0. \quad (4.3.7)$$

This differential equation is easily solved by separation of variables (and upon noting from Landau theory that the coefficient $\frac{\alpha}{2} < 0$ for the purposes of the integration) to give

$$\eta(z) = \frac{2\sqrt{2|\alpha|}}{\sqrt{|b|}} \frac{e^{\frac{\sqrt{|\alpha|}}{\sqrt{2}}(\frac{z}{A}+c)}}{e^{\sqrt{2|\alpha|}(\frac{z}{A}+c)} - 1}, \quad (4.3.8)$$

Where we have taken the absolute values of α and b to ensure that $\eta(z)$ is positive and real as required. The constant arising from the integration can easily be found using the boundary condition for $z = 0$ to give

$$c = \frac{1}{\sqrt{2}\sqrt{\alpha}} \frac{1}{1 + \frac{1}{2} \left[\frac{\log(2\sqrt{2}\sqrt{\alpha})}{\log(\sqrt{b})} \right]}.$$

The distribution function $\eta(z)$ then results in chiral behaviour near the surface of an ordered magnetic crystal with these effects vanishing to zero as we enter the bulk.

The spiral nature of the magnetic order induced by this chiral energy in the surface region can also lead to further changes in behaviour. The spiral ordering can lead to an incommensurate spin density wave state which can further lead to a coupling between the magnetization and the electric polarization leading to multiferroic behaviour [12]. This suggests that near a surface both magnetic and ferroelectric order coexist, enabling the control of magnetic properties by the application of magnetic fields or vice versa [2].

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5 Apendix

5.1 Schedule of Meetings with Supervisor

06/10/11:General introductory discussion about direction of project. Set several papers to read regarding surface effects and Dzyaloshinsky-Moriya interactions

13/10/11, 20/10/11, 27/10/11 & 03/11/11:Discussed the content of the papers from first meeting specifically with a view to fully understanding the mathematical techniques involved.

17/11/11, 24/11/11, 01/12/11, 08/12/11 & 15/12/11:Began to discuss papers more specifically related to Dzyaloshinsky-Moriya interactions induced by symmetry breaking at a surface, the nature of these interaction and the idea of finding the form of the distribution function determining how far they might propogate into the bulk.

19/01/12, 26/01/12 & 09/02/12:Discussed possibility of the introduction of spiral magnetism and consequences. First attempt to mathematically represent spiral magnetism using spherical polar co-ordinates.

16/02/12:After attempting to describe spiral state using spherical polar coordinates, approach resulted in free energy in the form of an expression with over 40 terms which I could not simplify.

27/03/12:Discussed a paper relating to chiral symmetry breaking in magnetic systems. Introduced possibility of solving problem faced with before the easter break by using Lifshitz invariants.

05/04/12, 12/04/12, 26/04/12 & 03/05/12:General progress updates on my research into Lifshitz invariants and Dzyaloshinsky’s paper on symmetry arguments.

17/05/12 & 28/05/12:Discussed approach to mathematically deriving the distribution function η and other details such as the form that the Lifshitz invariant should take.

31/05/12 & 06/06/12:Met to discuss progress and to get assistance with mathematical derivation of the form of the distribution function η . Also discussed progress on final

report so far.

07/06/12:Discussed feedback on final report so far.