# MAGNETIC DOMAINS IN HEMATITE

A thesis

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By

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## Abstract

The aim of the research in this thesis was to determine by all means available the magnetic domain structure of synthetic single crystal hematite and any other related properties. The magnetic domain structure was determined by the magnetite colloid technique. Ideally, it was 180° slab-type structure with the walls parallel to the basal plane. Magnetoelastic interactions with strain causing crystal defects produced distortions from this in the bulk crystal structure to maze-like or cylindrical 180° domains with parallel axes in the basal plane which changed direction if magnetoelastic interactions demanded it. In thin sections, the magnetoelastic effect caused the appearance of a two phase domain structure of $2\phi < 180^\circ$ walls where $\phi$ varied. The plane of these walls was parallel to basal plane easy direction and at $\sim 26^\circ$ to the basal plane. A 180° structure could disappear abruptly or more generally by these $2\phi$ walls. Magnetoelastic interactions with regular lattice distortions caused by the growth structure appeared to stabilize a narrow strip domain pattern of $2\phi$ walls in bulk (110) surfaces.

The magnetic domain observations also allowed the

Morin transition process to be observed. A colloid wall formed at the boundary between the antiferromagnetic-weakly ferromagnetic phases. The transition always occurred by a process of adjacent (110) growth layers going through the transition in succession as temperature varied. The transition temperature range was consistent with bulk measurements and was found to be caused by a non-uniform doping which also followed the growth structure. The shift was also related to difference of dopant ionic size from the Fe ionic size. Domain behaviour in this process appeared to be nothing more than a response to a changing boundary of the ferromagnetic phase. The domain structure generally showed a little or no changes in the process.

Mössbauer, magnetometer and crystal physical property measurements gave further support to the models proposed for the domain and transition behaviour.

Wall models consistent with magnetoelastic anisotropy were developed which explained the domain walls. Domain wall energies were calculated to be $\sim 4\text{-}13 \times 10^{-2}$ ergs/cm$^2$ which agreed with domain observations.

## Acknowledgements

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## I. Introduction

Hematite, or $\alpha$-$Fe_2O_3$, which is readily obtainable in large single crystals from nature, has a very weak magnetization at room temperature. Thus, in the past considerable research, has been devoted to the magnetic properties of hematite. This was, no doubt, stimulated by the research of Morin[1] and of Shull et al[2]. In 1950, Morin observed that hematite underwent a transition, now called the Morin transition, where the susceptibility rapidly increased with temperature. The Morin transition temperature $T_M$ has now been measured to be $T_M \sim -10$ C for very pure synthetic single crystal hematite. Then in 1951, Shull et al determined that hematite existed in what appeared to be two different antiferromagnetic states above and below the transition. In the next few years various researchers attempted to explain the weak moment in terms of crystal defects, impurities and even a net moment generated in antiferromagnetic domain walls. Finally, Dzialoshinskii[3] produced the now accepted thermodynamic argument which showed that in the one antiferromagnetic state it was possible for the sublattice spins to be slightly canted towards each other without lowering the magnetic symmetry. The quantum mechanical basis of this canting was subsequently given by Moriya[4] as a spin-orbit effect in the super-exchange interaction. Continued interest in hematite up to the present time has mainly been concerned

with measurement and explanation of effects related to magnetocrystalline anisotropy and magnetostriction.

Since hematite has an ordered ferromagnetic component, although very weak, a domain structure could be expected to exist. This was indeed shown to be the case by Blackman et al[5] and William et al[6] and has now been well established by the continued work by various researchers[7-11] under M. Blackman. Also, it has been established that the domain structure disappears in a characteristic fashion at the Morin transition.

Since we have a supply of, and could grow, large highly perfect,[12] pure and doped, crystals of hematite by a method established by P.J. Besser[13] it was felt that we might be able to contribute towards further explanation of the domain structure of hematite. Therefore, it is the purpose of this thesis, to put forward all the results of a research program into the domain structure in hematite.

## II. Preliminary Considerations

### A. The Magnetic Free Energy

Domain structures in ferromagnetic materials are a mechanism by which the magnetic free energy can be minimized. Therefore, to explain domain structures a knowledge of the mechanisms that can contribute to the magnetic free energy is necessary. The magnetic free energy can be expressed[14]

$$F_T = F_H + F_D + F_e + F_K + F_\sigma + F_o \qquad (1)$$

where $F_H$ is the free energy due to an applied magnetic field, $F_D$ the self energy due to uncompensated poles, $F_K$ the magnetocrystalline anisotropy energy, $F_\sigma$ the magnetostrictive energy, $F_e$ the exchange energy and $F_o$ the energy due to any other magnetic interactions relevant to the material such as crystalline imperfections. Thus, this expression is completely general and can be applied to any magnetically ordered material if the form of all the magnetic interactions is known.

The energy due to an applied field $\underline{H}$ is

$$F_H = -\int \underline{m}.\underline{H}dv \qquad (2)$$

and the self magnetostatic energy is

$$F_D = -\tfrac{1}{2}\int \underline{m}.\underline{H}_D dv \qquad (3)$$

where $\underline{m}$ is the magnetization and $\underline{H}_D$ is the self field due to uncompensated poles. For a uniformly magnetized ellipsoid

$$F_D = \tfrac{1}{2}Dm^2 \qquad (4)$$

where D is a geometrical factor depending on the shape of the ellipsoid relative to the direction of magnetization

and is relatively easy to calculate.[14] However, calculation of demagnetization energies for other than ellipsoid shaped specimens becomes very complicated and laborious and usually involves approximations.

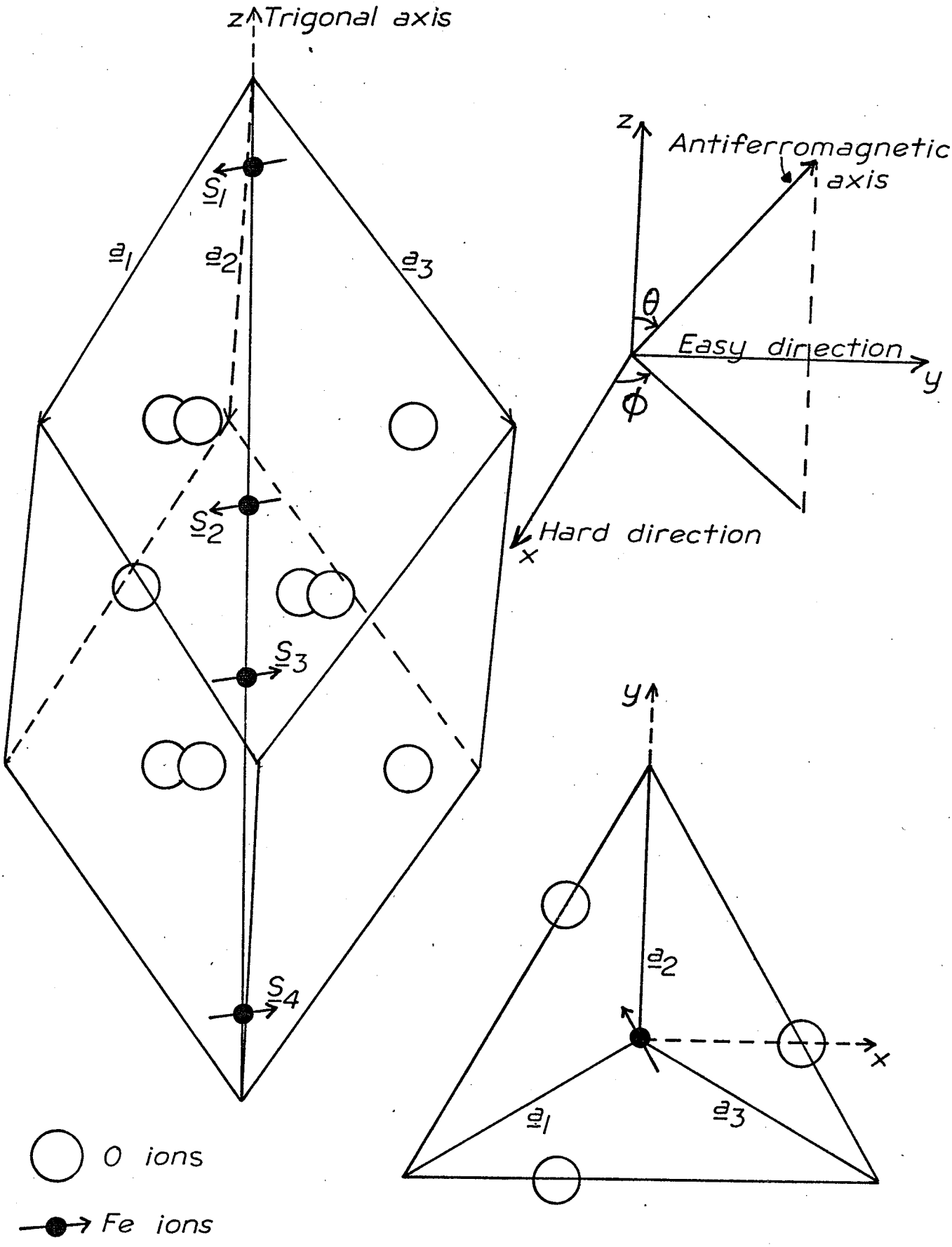
The remainder of the terms in equation (1), ignoring $F_o$, generally depend on crystal and magnetic symmetry. Therefore, a discussion of the crystal structure of hematite is appropriate at this point.

Hematite has a trigonal structure with space group $R\bar{3}c$ as determined by Pauling et al[15] and later refined by Blake et al.[16] The structure can be represented either by a rhombohedral or a hexagonal lattice. The rhombohedral cell is illustrated in Fig. 1. The structure may be described as a slightly distorted hexagonal close packed structure of oxygen atoms with 2/3 of the octahedral interstices containing iron atoms. The iron atoms are so arranged such that, along any hexagonal axis, every third interstice is empty. Therefore, the lattice repeats itself after every six layers of oxygen atoms.

The microscopic origin of ordering in magnetic systems is the exchange interaction.[17] This interaction arises between neighbouring magnetic ions because of the effect of the Pauli Exclusion Principle and the indistinguishability of electrons when the outermost electron orbitals of the two ions overlap. This generally results in the ions having

Figure 1.

Rhombohedral unit cell of hematite. The relative direction of the spins and the coordinate system to which they will always be referred are indicated on the unit cell.


z Trigonal axis
$\underline{S}_1$
$\underline{a}_1$
$\underline{a}_2$
$\underline{a}_3$
$\underline{S}_2$
$\underline{S}_3$
$\underline{S}_4$
z
Antiferromagnetic axis
θ
Easy direction
y
φ
x Hard direction
y
$\underline{a}_2$
x
$\underline{a}_1$
$\underline{a}_3$
O ions
Fe ions

parallel spin configurations as the lowest energy state. This interaction energy between the spins of the ions summed over the whole crystal can be represented, assuming only nearest neighbour interactions and isotropy of the exchange interaction as

$$F_e = -2J_e \sum \underline{S}_i \cdot \underline{S}_j \qquad (5)$$

$J_e > 0$ is the exchange integral and $\underline{S}_i$ the sum of the unpaired spins on the ion.

The exchange interaction may also occur via an intermediate non-magnetic ion such as oxygen as in the case of hematite. This interaction is now called superexchange and the quantum mechanical formalism has been developed by Anderson[17]. For cases where superexchange is appreciable the direct exchange is negligible since the magnetic ions are too widely separated. Therefore, in hematite, appreciable overlap occurs between the p electron states of the $O^{--}$ ion and the outer d electron states of the $Fe^{+++}$ ion. In the $O^{--}$ ground state the two p electrons are antiparallel. Therefore, if the d electron states on two magnetic ions have appreciable overlap with the same $O^{--}$ ion, the spins have an antiparallel configuration as the lowest energy state. Since the p state is dumbbell shaped this interaction is appreciable only if the Fe-O-Fe bond are appreciably different from $90^{o}$. According to Gilleo[18], for each Fe ion, there are nine appreciable interactions in hematite. Thus, the magnetic moments of the iron ions are orientated

in two antiparallel sublattices formed by alternate layers of ions parallel to the basal plane ((111) plane in rhombohedral representation).

Phenomenalogically this interaction may be represented in the molecular field approximation[14] by

$$\lambda \underline{M}_1 . \underline{M}_2 \qquad (6)$$

where $\underline{M}_1$ and $\underline{M}_2$ are the sublattice magnetizations and $\lambda$ is the exchange constant. Then $\lambda \underline{M}_1$ represents the molecular field of one sublattice acting on the other. There is no evidence to suggest that there is anything but a negligible exchange interaction between spins of the same sublattice.

In some basically antiferromagnetic materials with sufficiently low symmetry, such as hematite, Dzialoshinskii showed by a thermodynamic argument that it was possible for the sublattices to cant towards each other without lowering the symmetry of the magnetic state. If the thermodynamic potential of a magnetic state is expanded in terms of spin variables, then under the magnetic symmetry group for the antiferromagnetic axis in the basal plane, terms of the form

$$l_x m_y - l_y m_x \qquad (7)$$

are allowed. The vector $\underline{l} = (l_x, l_y, l_z) = \underline{S}_1 + \underline{S}_2 - \underline{S}_3 - \underline{S}_4$ defines the antiferromagnetic spin axis and the vector $\underline{m} = (m_x, m_y, m_z) = \underline{S}_1 + \underline{S}_2 + \underline{S}_3 + \underline{S}_4$ is the net magnetic moment. The spin vectors $\underline{S}_i$ and the cartesian coordinate system to which all calculations will be referred are illustrated

on the rhombohedral unit cell in Fig. 1. The interaction can be expressed in the molecular field approximation by

$$\underline{\mathcal{D}}.(\underline{M}_1 x \underline{M}_2) \qquad (8)$$

where $\underline{\mathcal{D}}$ is the Dzialoshinskii canting vector parallel to the [111] axis.

The microscopic origin of this interaction was formulated by Moriya[4] who extended the formalism of Anderson[17] to include spin-orbit effects in the superexchange interaction. This leads to an anisotropic term whose form is exactly similar to that of the molecular field approximation. Thus, the total exchange energy in hematite can be expressed, for the antiferromagnetic axis in the basal plane, as

$$F_e = \lambda \underline{M}_1.\underline{M}_2 + \underline{\mathcal{D}}.(\underline{M}_1 x \underline{M}_2) = \lambda M^2 \cos 2\theta + \mathcal{D} M^2 \sin 2\theta \qquad (9)$$

where $\theta$ is the canting angle and $|\underline{M}_1| = |\underline{M}_2| = M$ is the sublattice magnetization. Minimizing $F_e$ with respect to $\theta$ gives the canting angle as

$$\theta_{\mathcal{D}} = \frac{\mathcal{D} M}{2 \lambda M} = \frac{H_{\mathcal{D}}}{2H_e} \qquad (10)$$

where $H_e$ is the exchange field and $H_{\mathcal{D}}$ is the canting field. For pure hematite, resonance experiments[19,20] give values of $\mathcal{D} M \sim 2.2 \times 10^4$ Oe and from susceptibility measurements[21,22] $\lambda M \sim 10^7$ Oe. Thus, the canting angle is $\theta_{\mathcal{D}} \sim 1.1 \times 10^{-3}$ radians. The spontaneous moment $m = 2M\theta_{\mathcal{D}}$, from static measurements[23,24] has values ~2.0 emu/cc. A value of M = 880 emu/cc obtained by Mössbauer technique,[24] gives a value of m

~2.1 emu/cc which agrees with the static measurements.

Phenomenologically, the magnetocrystalline anisotropy energy $F_K$ can be expressed[20] as

$$F_K = K_1\sin^2\theta + K_2\sin^4\theta + K_3'\sin^6\theta + K_3\sin^6\theta \cos 6\phi \quad (11)$$

where $\theta$ is the angle the antiferromagnetic axis makes with the z axis and $\phi$ is the angle the projection of the antiferromagnetic axis in the x-y plane makes with the x axis. The first three terms are the uniaxial components and the last term is the three fold basal plane anisotropy. Microscopic origins for these anisotropies come from two main sources[25,26]; the magnetic dipolar anisotropy and the single ion anisotropy due to spin-orbit effects. Neglecting the contributions to the 3 fold basal plane anisotropy the contribution of the magnetic dipolar anisotropy was calculated to have an effective field value $H_{MD}\sim -10^4$ oe at absolute zero which favours the antiferromagnetic axis parallel to the trigonal axis. However, the uniaxial contribution from the single ion anisotropy favours the basal plane orientation of the antiferromagnetic axis. It is the competition between these two anisotropies which produce the Morin transition. Thus, at the Morin transition the effective field value of the uniaxial part of the single ion anisotropy $H_{SI} = -H_{MD}$ and therefore, in the neighbourhood of the transition $H_{SI}\sim|H_{MD}|$. The effective uniaxial anisotropy field above is

then $H_{SI}-|H_{MD}|$. From spin flop data[20] $H_{K_1} = H_{SI}-|H_{MD}| = 217$ Oe at $0^{o}K$. Therefore, in the temperature range of interest between the Morin transition and room temperature, $0 < H_{K_1} < \sim 1000$ Oe gives a value for $K_1 = MH_{K_1}$ in the range 0 to $10^6$ ergs/cm$^3$.

The basal plane anisotropy field has been measured by microwave resonance[20,27] to have an effective field value $\sim 1.1$ to $1.8 \times 10^{-2}$ Oe. Therefore, the value of $K_3 = \frac{MH_{K_3}}{18}$ is $\sim 0.5$ to 1.0 ergs/cm$^3$.

In general every magnetic state induced or spontaneous is accompanied by an anisotropic deformation of the crystal called magnetostriction. This deformation will exhibit the same symmetry as the crystal space group. Linear magnetostriction is the deformation induced by an applied magnetic field. In hematite, it was observed and measured by Anderson et al[28] for the purely antiferromagnetic state in hematite. Piezomagnetism, the inverse of linear magnetostriction has been discussed and also observed by various researchers.[29] However, the effect that is important to the domain properties is the spontaneous magnetostriction associated with the direction of the antiferromagnetic axis. The spontaneous magnetostriction can be found by minimizing the sum of the elastic energy and the magnetoelastic energy. The resulting equilibrium strain deformation is the spontaneous magneto-

striction. The elastic and magnetoelastic coupling coefficients are fourth order polar tensors and the energies associated with them are[27,30] respectively

$$E_e = \tfrac{1}{2}C_{11}e_{xx}^2 + C_{12}e_{xx}e_{yy} + C_{13}e_{xx}e_{zz} + 2C_{14}e_{xx}e_{yz} + \tfrac{1}{2}C_{11}e_{yy}^2 + C_{13}e_{yy}e_{zz} - 2C_{14}e_{yy}e_{yz} + \tfrac{1}{2}C_{zz}e_{zz}^2 + 2C_{44}e_{yz}^2 + 2C_{44}e_{xz}^2 + 2C_{14}e_{xz}e_{yz} + (C_{11} - C_{12})e_{xy}^2 \qquad (12)$$

and

$$E_{me} = B_{11}\gamma_x^2 e_{xx} + B_{12}\gamma_x^2 e_{yy} + B_{14}\gamma_x^2 e_{yz} + B_{12}\gamma_y^2 e_{xx} + B_{11}\gamma_y^2 e_{yy} - B_{14}\gamma_y^2 e_{yz} + B_{zz}\gamma_z^2 e_{zz} + B_{41}\gamma_y\gamma_z e_{xx} - B_{41}\gamma_y\gamma_z e_{yy} + B_{44}\gamma_y\gamma_z e_{yz} + B_{44}\gamma_x\gamma_z e_{xz} + 2B_{41}\gamma_x\gamma_z e_{xy} + 2B_{14}\gamma_x\gamma_y e_{xz} + 2(B_{11} - B_{12})\gamma_x\gamma_y e_{xy} \qquad (13)$$

where $C_{ij}$, $B_{ij}$, $e_{ij}$ and $\gamma_i$ are the elastic constants, the magnetoelastic coupling constants, the strains and the direction cosines of the antiferromagnetic axis respectively. Then by forming $\frac{\partial}{\partial e_{ij}} (E_e + E_{me}) = 0$, a set of equations is obtained from which the equilibrium strains can be found. Assuming the spin axis is constrained to the basal plane then the solutions to the equilibrium strains[27], after correcting them[30] to give the exact solution, are:

$$e_{xx} = \frac{C_{33}(B_{11} + B_{12}) + 2C_{13}B_{33}}{2\left[C_{33}(C_{11} + C_{12}) - 2C_{13}^2\right]} + \frac{\left[C_{14}B_{14} - C_{44}(B_{11} - B_{12})\right]}{2\left[C_{44}(C_{11} - C_{12}) - 2C_{14}^2\right]}\cos 2\phi$$

$$= M + N\cos 2\phi$$

$$e_{yy} = M - N\cos 2\phi \qquad (14)$$

$$e_{zz} = \frac{C_{13}(B_{11} + B_{12}) + (C_{11} + C_{12})B_{33}}{C_{33}(C_{11} + C_{12}) - 2C_{13}^2} = K$$

$$e_{xy} = N\sin 2\phi$$

$$e_{xz} = \frac{\left[2C_{14}(B_{11} - B_{12}) - (C_{11} - C_{12})B_{14}\right]}{4\left[C_{44}(C_{11} - C_{12}) - 2C_{14}^2\right]}\sin 2\phi = L\sin 2\phi$$

$$e_{yz} = L\cos 2\phi$$

Physically this deformation can be interpreted[27] as consisting of three parts; firstly, a uniform deformation independent of the antiferromagnetic axis direction, secondly, a