MAGNETOSTRICTION IN FERROMAGNETS
AND ANTIFERROMAGNETS

by

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ABSTRACT

Magnetostriction and thermal expansion measurements were performed on the antiferromagnets Cr$_2$O$_3$ and MnF$_2$ and on the ferromagnet EuS. A high-sensitivity capacitance technique was used. The data were used to test the theory of exchange magnetostriction, and to determine the phase boundaries (in the H-T plane) of the two antiferromagnets. The phase boundaries were compared with a recent theory of bicritical points which is based on scaling and renormalization group analyses.

The transitions between the three magnetic phases of the uniaxial antiferromagnet Cr$_2$O$_3$ were investigated in magnetic field H up to 180 kOe (H|| easy-axis) and at temperatures T between 4.2 K and the Neel temperature $T_N=307.4\pm0.2$ K. An abrupt length-change along the easy-axis accompanied the spin-flop transition. This length-change amounted to $\delta l/l=(3.5\pm0.4)\times10^{-5}$ at $T=4.2$ K and it decreased monotonically towards zero as $T$ was raised towards the bicritical temperature $T_b$. These length-changes were used to determine the spin-flop transition field $H_{SF}(T)$. This field increased monotonically, from $H_{SP}(4.2\ K)=(59.3\pm1.5)$kOe, as $T$ was raised towards $T_b$. λ-like anomalies in the thermal expansion coefficient $(1/l)(\partial l/\partial T)_H$ accompanied both the antiferromagnetic-to-paramagnetic (AF-P) and spin-flop-to-paramagnetic (SF-P) phase transitions. From these anomalies, the AF-P and SF-P phase boundaries were determined for $H<180$ kOe. These boundaries were compared to recent scaling theories developed by Fisher, Nelson, and Kosterlitz for the shape of the phase boundaries in the vicinity of the bicritical point, $(T_b,H_b)=([T_N-(0.485\pm0.03)K], (120.0\pm0.5)$kOe).
Good qualitative agreement was obtained. Quantitative comparisons indicated that to obtain the best agreement between experiment and theory, an orthorhombic (rather than cylindrical) symmetry for the anisotropy had to be assumed. An alternative to this assumption is that the theoretical estimate for the location of the best scaling axes must be modified.

The AF-P and SF-P phase boundaries of the uniaxial antiferromagnet MnF$_2$ were determined in magnetic fields $H$ up to 140 kOe ($\mathbf{H} ||$ easy-axis, [001]). $\lambda$-like anomalies in the thermal expansion coefficient $(1/\lambda)(\partial\lambda/\partial T)_{\Omega}$ were used to determine points on both the AF-P and SF-P phase boundaries. In addition, points on the AF-P line were determined from $\lambda$-like anomalies in the derivative $[\partial(\Delta\lambda/\lambda)/\partial H]_T$ of the magnetostriction. Good qualitative agreement was obtained between the experiments and the predictions of the scaling theory for the shape of the boundaries in the vicinity of the bicritical point $(T_b, H_b) = (64.81 \pm 0.07$ K, $119.3 \pm 0.8$ kOe). However, as in the experiments on Cr$_2$O$_3$, quantitative comparisons suggested that MnF$_2$ has sufficient anisotropy within the (001) plane to invalidate the modelling of the crystal as a pure uniaxial material, at least for the purposes of the bicritical scaling theory.

The longitudinal and transverse magnetostrictions along the [001] direction of the ferromagnet EuS were measured at temperatures between the Curie temperature $T_C = (16.49 \pm 0.04$) K and $146$ K in magnetic fields up to 140 kOe. The volume magnetostriction was obtained from these measurements. The data indicated that above $T_C$ the isotropic magnetostriction (independent of the direction of $H$) was much larger than the anisotropic magnetostriction. The isotropic magnetostriction was attributed to the volume dependence of the nearest-neighbor and next-nearest-neighbor exchange constants, $J_1$ and $J_2$. The results were compared to the theory of Callen and Callen. Assuming only nearest- and next-nearest neighbor exchange interactions, this theory relates the isotropic magnetostriction to the $H$-dependence of the two-spin correlation functions $\langle S_1 \cdot S_2 \rangle_{nn}$ and $\langle S_1 \cdot S_2 \rangle_{nnn}$ for nearest and next-nearest neighbors, respectively. Based on these theoretical results for the magnetostriction, numerical predictions were obtained using high-temperature series expansions. These numerical results point to the inadequacy of the Mean-Field Approximation, particularly near $T_C$. The overall agreement between experiment and theory (evaluated using series expansions) is good. However, there are discrepancies near $T_C$ which suggest that for EuS the model of a Heisenberg ferromagnet with only nearest- and next-nearest-neighbor exchange interactions is good but not exact.

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Magnetic Materials and Magnetic Interactions

The study of materials under the influence of a magnetic field results in a large variety of types of behavior. Among all materials it is possible to identify certain classes of materials which can be understood in terms of relatively simple models. This thesis reports on certain aspects of the behavior of two of these classes--ferromagnets and antiferromagnets--as realized in experiments performed on three materials--MnF$_2$ and Cr$_2$O$_3$ (antiferromagnets) and EuS (a ferromagnet).

The magnetic properties of a substance are mainly due to the electrons contained in the material, their response to an external magnetic field, and their interactions with other electrons. Of particular significance in magnetic materials are the electrons in partially filled shells. According the Hund's rule, the assignment of electrons to the orbitals in an unfilled shell is done in such a way that the total spin $S$ is a maximum and the total angular momentum $L$ is the largest which allows for this $S$. As a consequence, an atom may have a magnetic moment of order $\mu_B$, the Bohr magneton, and materials
containing such atoms are expected to have significant magnetic properties.

Elements which may have such unfilled shells are the transition elements (such as Cr, Fe, and Ni which have partially filled inner d-shells), the rare earth elements (lying between cerium and ytterbium and possessing partially filled 4f-shells) and the actinide elements (with unfilled 5f-shells). This is true both for separate atoms of these elements, and also for atoms of these elements which are present in a solid. When these elements form molecules, the inner partially filled orbitals will often not take part in the bonding and hence the ions will retain their magnetic properties.

In what follows, we specialize to the case of insulating ionic crystals containing ions with unfilled shells. The magnetic properties of such materials are expected to be primarily due to the presence of the magnetic moments localized on the magnetic ions, and the interactions of these moments with each other and with the external magnetic field. Further, materials with only a single species of magnetic ion are considered.

The Hamiltonian describing the full many-electron problem represented by these ionic crystals is usually reduced to an effective Hamiltonian for the localized spins. Terms up to second order (and sometimes higher) in the spin operators are retained, resulting in a model which can explain most of
the observed features of real ferromagnetic and antiferromagnetic materials.

**Magnetic Order**

At zero temperature and zero magnetic field, the interactions between the magnetic moments can result in a long-range magnetic order. For example, if the interactions between magnetic moments favors parallel alignment, a ferromagnetic ordering can take place in which all the moments point in the same direction. However, if the dominant interaction between magnetic moments favors an antiparallel orientation of adjacent atoms, an antiferromagnetic order can take place in which the spins point upwards and downwards in some alternating fashion throughout the crystal.

In certain crystal structures (such as simple cubic or body-centered cubic) the lattice formed by the magnetic ions can be divided into two identical sublattices with the nearest neighbors of an atom in one sublattice being in the other sublattice. An antiferromagnetic ordering can then take place in which all the magnetic moments in one sublattice are oriented parallel to each other but antiparallel to the moments in the other sublattice. A material which exhibits such an ordering is often called a "simple antiferromagnet."

In general, any magnetic ordering will persist over a range of temperature and field, the degree of ordering being modified by the thermal agitation and the forces on the
magnetic ions due to the field. The concept of an order parameter is introduced to measure the degree of ordering.

In a ferromagnetic material at zero magnetic field, the order parameter is the total magnetization $\mathbf{M}$. At zero temperature $T=0$, $|\mathbf{M}|$ will take on its maximum value $M_S$, the saturation magnetization. All the magnetic moments are lined up pointing in the same (crystallographic) direction $\mathbf{M}/|\mathbf{M}|$. As the temperature is raised, the thermal agitation will decrease the value of $|\mathbf{M}|$ until a temperature is reached (the Curie temperature $T_C$) when $|\mathbf{M}|$ becomes zero. Above $T_C$ there is no net ferromagnetic long-range order and the order parameter $\mathbf{M}$ stays equal to zero.

In a simple antiferromagnetic material with sublattice magnetizations $\mathbf{M}_1$ and $\mathbf{M}_2$, the order parameter is $\mathbf{L}=\mathbf{M}_1-\mathbf{M}_2$. A net antiferromagnetic order exists when $\mathbf{L}\neq 0$. Increasing the temperature (which thermally disorders both sublattices) and/or increasing the magnetic field (which tends to line up both sublattice magnetizations parallel to $\mathbf{H}$) will decrease the magnitude of $\mathbf{L}$. When $\mathbf{L}$ becomes zero, the distinction between the two sublattices disappears and the antiferromagnetic long-range order no longer exists. At zero field, this occurs as the temperature is increased through the Néel temperature $T_N$.

**Exchange Energy**

The dominant interaction between the magnetic moments in such a crystal is usually the exchange interaction which originates from the Pauli principle's requirement that the wave
function of a system of electrons be antisymmetric under the exchange of the space and spin coordinates of any two electrons. As a result, the eigenvalues of the system will depend on the relative orientation of each spin with respect to its neighbors. The interaction may be a direct one between the two ions or it may be indirect, proceeding via the non-magnetic ions between the magnetic atoms. In most cases, the interaction is isotropic (or largely so) depending solely on the relative orientation of two spins and not, for example, on the orientation of the spins relative to the line joining them. The isotropic exchange interaction will thus determine the orientation of the spins with respect to each other, but will not favor any orientation of the spins with respect to the crystal axes.

This isotropic exchange interaction is often described by a term in the effective Hamiltonian of the form \(-2J_{ij}\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j\), the Heisenberg exchange term, for each distinct pair of spins \(i\) and \(j\) in the material. \(J_{ij}\) is the exchange constant linking the spins \(i\) and \(j\). \(J_{ij} > 0\) favors a parallel orientation (ferromagnetic alignment), and \(J_{ij} < 0\) favors an antiparallel orientation (antiferromagnetic alignment). It is usually the case that the magnitude of \(J_{ij}\) falls off rapidly with increasing separation \(r_{ij}\) between the spins, and only the nearest (and perhaps the next-nearest) neighbor exchange need be considered. Furthermore, the crystal symmetry assures that the exchange constants for equivalent pairs of spins are equal. In a
crystal with only a single species of magnetic ion and only nearest-neighbor exchange, we can write the effective spin Hamiltonian as

\[ H = -2J \sum_{<ij>} \mathbf{S}_i \cdot \mathbf{S}_j - g\mu_B \mathbf{H} \cdot \mathbf{S}_i \]  

where the sum \( <ij> \) proceeds over all distinct nearest neighbor pairs, \( J \) is a single exchange constant, and the second term is the Zeeman energy of the spin system in an external magnetic field \( \mathbf{H} \). \( g \) is the g-factor and \( \mu_B \) the Bohr magneton.

**Anisotropy Energy**

The isotropic Heisenberg Hamiltonian is sufficient to explain many of the observed properties of real magnetic materials (at least qualitatively), but more realistic models must include further interaction terms. For example, the exchange Hamiltonian cannot explain the preferred alignment of the ordered spins with respect to the crystalline axes (as distinguished from their alignment with respect to each other). The interaction which favors a particular orientation of the spins relative to the crystal axes is known as anisotropy, and arises from three main sources: the crystal field, the classical magnetic dipole-dipole interaction, and the anisotropic exchange.

When a free magnetic ion is brought into the crystalline electric field (produced at its lattice site by the neighboring ions), the directional degeneracy of the orbital
angular momentum is removed, partially or completely, due to the crystalline Stark effect. This has two major effects. First, this lifting of degeneracy may lead to a "quenching" or partial "quenching" of the angular momentum—the ground state of an ion in a crystal will not be a pure angular momentum state. (The $z$-component $L_z$ of the orbital angular momentum will no longer be a good quantum number.) For complete quenching, the ion will have an average orbital angular momentum $|\bar{L}| = 0$. As a result, the magnetic moment of the ion will be due mainly to the spin angular momentum. The magnetic moment of an ion will then be given by $\vec{\mu} = g_\mu_B \vec{S}$ where $g$ is very close to the spin only-value of $g = 2$. This effect is especially strong in the transition elements since the d-orbitals extend far from the nucleus. The effect is much smaller in the rare earth ions where the 4f orbitals are deep in the ion and shielded from the crystal field by the outer electrons.

Secondly, because of the LS coupling, the energy of a magnetic moment will depend on the orientation of the moment with respect to the crystalline axes. This gives rise to a one-ion anisotropy—a term in the effective Hamiltonian depending on the orientation of a single spin (independent of the behavior of all the other spins).

For an S-state ion (such as Mn$^{++}$ and Eu$^{++}$) in which the orbital wave function is spherically symmetric, the anisotropy due to the crystal field is very small.
The crystal field results in a one-ion anisotropy. The other two mechanisms result in a two-ion anisotropy. The isotropic exchange interaction can be generalized to include anisotropic effects by writing, instead of $J_{ij} \hat{S}_i \cdot \hat{S}_j$, a sum of the form $\sum \sum J_{ij}^{\mu \nu} S_i^\mu S_j^\nu$ where $J_{ij}^{\mu \nu}$ is a tensor and the indices $\mu$ and $\nu$ refer to the three components of the appropriate spin. The classical magnetic dipole-dipole interaction between two magnetic moments $\hat{\mu}_i$ and $\hat{\mu}_j$ can be written as

$$\frac{\hat{\mu}_i \cdot \hat{\mu}_j}{r_{ij}^3} = 3 \frac{(\hat{\mu}_i \cdot \hat{r}_{ij})(\hat{\mu}_j \cdot \hat{r}_{ij})}{r_{ij}^5} \quad (1.2)$$

where $\hat{r}_{ij}$ is the separation between the ions. Using the definition of $\hat{\mu}_i = \mu_B \hat{g} \cdot \hat{S}$ where $\hat{g}$ is the (possibly anisotropic) $g$-factor, the reduction to the generalized form follows. The dipole-dipole interaction is usually much weaker than the isotropic exchange, but because of the long range of the forces, it can sometimes be important.

The anisotropic exchange interaction arises from an LS coupling and an isotropic exchange interaction through the excited states. The crystal field mixes states with different $L_z$ values so that there will be non-zero off-diagonal terms in the LS coupling. These off-diagonal terms combined with an isotropic exchange interaction will result (in third order perturbation theory--second order in the LS coupling and first order in the exchange) in the anisotropic exchange terms.
These terms are particularly important in ferromagnetic metals, but less so in the materials considered here.

The form of the one-ion anisotropy energy is restricted by symmetry considerations imposed by the crystal structure. A simple type of anisotropy (if the symmetry allows it) is the uniaxial (cylindrical) one in which there is a special axis \( \hat{n} \) with the anisotropy being a function only of the angle between a spin \( \vec{S} \) and the special axis (i.e., a function of \( \hat{n} \cdot \vec{S} \) only). A uniaxial anisotropy of the easy-axis type is obtained when the anisotropy favors alignment of the spins parallel to this special axis. To second order in spin, this means a contribution to the Hamiltonian of the form

\[
-K \sum_i (\hat{n} \cdot \vec{S}_i)^2
\]

if the anisotropy can be cast in a one-ion form.

A two-ion anisotropy can sometimes be simulated by this form if the anisotropy constant \( K \) is taken to be temperature dependent. Such a procedure is often employed at the level of the free energy when a phenomenological form for the anisotropy is used.

In a cubic crystal, symmetry considerations do not allow such a simple form for the anisotropy. A situation which is often obtained in cubic ferromagnets is the existence of a set of crystallographically equivalent easy axes (for example, the three axes [001], [010], and [100] or the four axes [111], [\bar{1}11], [1\bar{1}1], and [11\bar{1}]). The spin system will tend to align parallel to one of the easy axes. A domain structure can occur when the orientation in different parts of
the crystal is along different axes. The lowest order (in the direction cosines of \( \hat{S}_i \) with respect to the crystal axes) single-ion anisotropy term which can occur in a cubic crystal is the fourth order. Often considered is an anisotropy energy of the form \(-K_1 \varepsilon \left( \alpha_{11}^2 \alpha_{12}^2 + \alpha_{12}^2 \alpha_{13}^2 + \alpha_{13}^2 \alpha_{11}^2 \right)\) where \( K_1 \) is the (cubic) anisotropy constant, and \( \alpha_{11}, \alpha_{12}, \alpha_{13} \) are the three direction cosines of \( \hat{S}_i \). When \( K_1 > 0 \), the easy axes are the [001] and equivalent axes. When \( K_1 < 0 \), the [111] and equivalent axes are the easy axes.

**Mean Field Approximation**

Including only a single-ion anisotropy \( H_{\text{Ai}}(\hat{S}_i) \), the effective Hamiltonian for the spin system is

\[
H = -2 \sum_{ij} J_{ij} \hat{S}_i \cdot \hat{S}_j - g \mu_B E \hat{S}_i + \sum_i H_{\text{Ai}}(\hat{S}_i). \tag{1.3}
\]

Statistical Mechanics provides a procedure for calculating physical properties from this Hamiltonian but, in general, the many-spin problem cannot be solved exactly and some approximations must be introduced in any theoretical treatment.

The simplest approximation, but one which retains a large amount of physics, is the Mean Field Approximation (MFA). It consists of focusing on a single spin \( i \) and calculating its properties assuming that all the other spins are fixed at their average values. For example, the average spin is, by Statistical Mechanics, given by
where the traces go over the \((2S+1)^N\) multi-spin states. \(N\) is the total number of spins, \(k\) the Boltzmann constant and \(T\) the temperature. The MFA consists in replacing all the \(\hat{S}_j, (j \neq i)\) by \(\langle \hat{S}_j \rangle\) leading to

\[
\langle \hat{S}_i \rangle = \frac{\text{tr}_i \hat{S}_i e^{-\hat{H}_{\text{eff}}/kT}}{\text{tr}_i e^{-\hat{H}_{\text{eff}}/kT}},
\]  

(1.5)

where now the traces \(\text{tr}_i\) go over the \((2S+1)\) states of the single ion \(i\) and where the effective one-spin Hamiltonian is

\[
\hat{H}^{(i)}_{\text{eff}} = -2\hat{S}_i \cdot \sum_{j \neq i} J_{ij} \langle \hat{S}_j \rangle - g\mu_B \hat{H}_i \hat{S}_i + H_{A_i} \langle \hat{S}_i \rangle
\]

(1.6)

\[
= -g\mu_B \hat{H}_{\text{eff}}^{(i)} \hat{S}_i + H_{A_i} \langle \hat{S}_i \rangle.
\]

and the effective field is defined to be

\[
\hat{H}_{\text{eff}}^{(i)} = \hat{H} + \frac{2}{g\mu_B} \sum_{j \neq i} J_{ij} \langle \hat{S}_j \rangle.
\]

(1.7)

The traces in Eq. (1.5) can be evaluated for an arbitrary \(\hat{H}_{\text{eff}}^{(i)}\).

For example, when \(H_{A_i} = 0\), Eq. (1.5) becomes

\[
\langle \hat{S}_i \rangle = S B_s \left[ g\mu_B S |\hat{H}_{\text{eff}}^{(i)}|/kT \right] \frac{\hat{H}_{\text{eff}}^{(i)}}{|\hat{H}_{\text{eff}}^{(i)}|},
\]

(1.8)
where $B_S(x)$ is the Brillouin function for spin $S$ and argument $x$. An equation similar to Eq. (1.5) holds for every spin in the system. In a ferromagnet, for which all ions are equivalent, $\langle S_1 \rangle = \langle S_j \rangle = \langle S \rangle$, and Eq. (1.5) becomes an identity which can only be satisfied by a suitable choice of $\langle S \rangle$.

In a two-sublattice antiferromagnet with all the ions in a sublattice equivalent, the spins in each sublattice will have a common value for their average spin. Eq. (1.5) will then give two equations in the parameters $\langle S_1 \rangle$ and $\langle S_2 \rangle$, the average spins for sublattice 1 and 2 respectively. These two equations must be solved self-consistently.

More complicated orderings (with more than two sublattices, for example) can be handled in a similar fashion.

The MFA gives a good qualitative picture of most of the fundamental properties of magnetic materials, such as the Curie-Weiss behavior of the susceptibility above $T_C$ or $T_N$ and the sublattice magnetizations and their temperature variation. It is useful for determining the types of magnetic order which are possible and the nature of the transitions between different types of magnetic order (i.e., phase transitions).

The most serious shortcoming of the MFA is its neglect of short range order. Many attempts have been made to improve on it.

The simplest improvements upon the MFA are the "cluster approximations." Cluster Approximations treat a small number of spins (for example, a pair of spins or a spin and all its
nearest neighbors) exactly, replacing the interactions with the rest of the lattice by an effective field. The qualitative (and some quantitative) effects of the short range order are thus included.

A more sophisticated approach, which often leads to quite accurate results, is based on high-temperature series expansions. In high-temperature series expansions, the exact expressions for a physical quantity (such as the free energy or the susceptibility) is expanded in powers of $1/T$. Such an expansion is valid only in the disordered (paramagnetic) phase. The coefficients of this series can be calculated exactly, an approximation coming in only when the series is truncated. By suitable extrapolation techniques, the range of application can be pushed fairly close to the ordering temperature.

Scaling theories are used to explain the behavior of physical quantities very close to critical points (such as the Curie temperature $T_C$ in a ferromagnet or the Néel temperature $T_N$ in an antiferromagnet). For example, near the Curie temperature of a ferromagnet, the magnetization $M(H,T)$ is expected to be given by

$$ M(H,T) \approx \left| 1 - \frac{T}{T_C} \right|^{\lambda_M} m\left( \left| 1 - \frac{T}{T_C} \right|^{\lambda_H} H \right) , $$

where $\lambda_M$ and $\lambda_H$ are critical exponents and $m(x)$ is a scaling function. By suitably scaling (with a power of $\left| 1 - T/T_C \right|$), the
magnetization $M$ and the magnetic field $H$, the behavior near $T_C$ has been reduced to a function of a single variable. The exponents $\lambda_M$ and $\lambda_H$ and the function $m(x)$ are expected to be common to a large class of materials.

Scaling theories are largely phenomenological in origin. The recently advanced renormalization theory starts with a microscopic Hamiltonian and leads to conclusions which agree with scaling theory. Renormalization theory attempts to calculate the parameters (exponents and scaling functions) for a given model Hamiltonian.

**Magnetostriction**

Magnetostriction is the change in a sample's dimensions caused by a magnetic field. It arises because of the dependence of the free energy upon both elastic strain and magnetic field. The equilibrium strains in a material are determined by the minimization of the free energy and will thus be dependent on the magnetic field. The principal magnetic energies which are strain dependent are the exchange energy, the anisotropy energy, and the magnetostatic energy. Each of these leads to a contribution to the measured magnetostriction.

Historically, and even at present, most experiments on the magnetostriction of magnetic materials are performed on ferromagnets at temperatures well below the ordering temperature (Curie temperature). In such situations, the material is almost completely ordered within each domain. Application of a magnetic field will change the degree of this order only
slightly. The magnetostrictive effects then arise from the alignment of the magnetic moments by the magnetic field. The exchange energy remains almost constant while the anisotropy and magnetostatic energies change appreciably. Thus, even though the exchange energy is much larger than the other energies, the magnetostriction in most experiments is dominated by the strain dependence of the anisotropy and magnetostatic energies.

Most of the work reported in this thesis is concerned with the magnetostriction above and near the ordering temperatures. The exchange energy is then sensitive to changes in T or H, just as the anisotropy and magnetostatic energies are. However, the changes in the exchange energy are much larger than in the other energies. Under these circumstances, the magnetostriction due to the strain dependence of the exchange energy swamps the contributions from the other energies (anisotropy and magnetostatic). Thus, it is the exchange magnetostriction which is of major importance in interpreting the experimental results presented.
CHAPTER II

PHASE DIAGRAM OF THE UNIAXIAL ANTIFERROMAGNET FOR $\hat{H} \parallel \hat{n}$

For the simple model of an easy-axis antiferromagnet [1], as outlined in the Introduction, the major features of the phase diagram (in the H-T plane) can be determined from calculations based on the molecular field approximation.

When a magnetic field $H$ is applied along the easy axis, $\hat{H} \parallel \hat{n}$, the phase diagram in the H-T plane, as sketched in Fig. (II.1), consists of three phases [2]: the paramagnetic (P) phase, the antiferromagnetic (AF) phase, and the spin flop (SF) phase. In the P phase, the sublattice magnetizations $\vec{M}_1$ and $\vec{M}_2$ are equal in both magnitude and direction and are oriented along $\hat{H}$. The antiferromagnetic order parameter $\vec{\mathcal{L}}$ is then equal to zero. The P phase exists at high temperatures and/or high magnetic fields when the antiferromagnetic exchange interaction is insufficient to cause any net antiferromagnetic long-range order. The other two phases exhibit a net antiferromagnetic order ($\vec{\mathcal{L}} \neq 0$).

In the AF phase, $\vec{M}_1$ and $\vec{M}_2$ lie along $\hat{n}$ or $-\hat{n}$, but are unequal in magnitude and/or are antiparallel. The order parameter is nonzero and is parallel to the easy axis, $\vec{\mathcal{L}} \parallel \hat{n}$. This is the normal antiferromagnetic phase seen at low magnetic
fields and for $T < T_N$. In the SF phase, which occurs at higher fields, $\mathbf{M}_1$ and $\mathbf{M}_2$ are equal in magnitude and form equal (non-zero) angles with $\mathbf{h}$. Their projections onto the plane perpendicular to $\mathbf{h}$ are antiparallel. Again, the order parameter is non-zero but in the SF phase $\mathbf{L} \parallel \mathbf{h}$.

The boundaries between the three phases meet at the bicritical point (or, as it has been called earlier, the triple point) $(T_b, H_b)$.

The AF-SF transition (spin-flop transition) is a first order transition. It is accompanied by discontinuous changes in the total magnetization $\mathbf{M}$ and in the magnetic entropy $\Omega$. The AF-P and SF-P are second order transitions wherein $\mathbf{M}$ and $\Omega$ are continuous across the boundary but their derivatives with respect to $H$ and $T$ exhibit $\lambda$-anomalies.

**AF-P Transition**

To demonstrate the procedure used in applying the MFA to the determination of phase boundaries and to exhibit qualitatively what should be seen experimentally as these boundaries are crossed, we consider the AF-P phase boundary in an easy-axis uniaxial antiferromagnet with $\mathbf{H} \parallel \mathbf{h}$ and with an exchange energy much larger than the anisotropy energy. Considering only the nearest neighbor exchange, the Hamiltonian is

$$\mathcal{H} = -2J \sum_{<ij>} \mathbf{S}_i \cdot \mathbf{S}_j - g\mu_B H \mathbf{S}_i \cdot \mathbf{h}, \quad (\text{II.1})$$
Fig. (II.1). Schematic phase diagram for a uniaxial antiferromagnet with weak anisotropy and $\vec{H} \parallel$ easy-axis. The arrows represent the magnetizations of the two sublattices.
where \(<ij>\) runs over all the distinct nearest neighbor pairs of spins. The small anisotropy assures that for small magnetic fields the spins will lie along \(\hat{n}\). It is assumed that this is the only effect of the anisotropy.

Applying the MFA to a simple antiferromagnet with two sublattices "1" and "2" and with the z nearest neighbors of any spin lying in the other sublattice, the one spin effective Hamiltonian as given by Eq. (I.6) and Eq. (I.7) is

\[
H_{\text{eff}}^{(1)} = -g\mu_B \hat{H}_{\text{eff}}^{(1)} \cdot \hat{s}_1 \quad \text{and} \quad H_{\text{eff}}^{(2)} = -g\mu_B \hat{H}_{\text{eff}}^{(2)} \cdot \hat{s}_1 ,
\]

where

\[
\hat{H}_{\text{eff}}^{(1)} = \hat{H} + \frac{2Jz}{g\mu_B} \langle \hat{s}_2 \rangle \quad \text{and} \quad \hat{H}_{\text{eff}}^{(2)} = \hat{H} + \frac{2Jz}{g\mu_B} \langle \hat{s}_1 \rangle
\]

and \(\langle \hat{s}_1 \rangle\) and \(\langle \hat{s}_2 \rangle\) are the average values for the spins in sublattices 1 and 2 respectively. Each spin precesses in its own effective field \(\hat{H}_{\text{eff}}^{(k)}\) independently of all the other spins (except that the averages \(\langle \hat{s}_1 \rangle\) and \(\langle \hat{s}_2 \rangle\) must be determined self-consistently).

For the general \(\hat{H}\), the \(\langle \hat{s}_k \rangle\) have their directions parallel to \(\hat{H}_{\text{eff}}^{(k)}\) and their magnitudes given by

\[
\frac{|\langle \hat{s}_k \rangle|}{S} = B_S \left( \frac{g\mu_B S}{kT} |\hat{H}_{\text{eff}}^{(k)}| \right),
\]

where \(B_S\) is the Brillouin function.
In the case of \( \vec{H} || \vec{\mathbf{a}} \), \( \langle \hat{S}_1 \rangle \) and \( \langle \hat{S}_2 \rangle \) will lie either parallel or antiparallel to \( \vec{\mathbf{a}} \) and the reduced sublattice magnetizations are

\[
\sigma_1(H,T) = \frac{\vec{a} \cdot \langle \hat{S}_1 \rangle}{S} = B_S \left( \frac{g_\mu_B S}{kT} \left[ H + 2JzS \right] \sigma_2 \right)
\]

(II.5)

\[
\sigma_2(H,T) = \frac{\vec{a} \cdot \langle \hat{S}_2 \rangle}{S} = B_S \left( \frac{g_\mu_B S}{kT} \left[ H + 2JzS \right] \sigma_1 \right)
\]

(II.6)

These equations must be solved self-consistently to obtain \( \sigma_1 \) and \( \sigma_2 \).

The antiferromagnetic order parameter \( \hat{L} \) is given by

\[
\hat{L} = \hat{\mathbf{M}}_1 - \hat{\mathbf{M}}_2 = \frac{N g_\mu_B S}{2} \left[ \sigma_1 - \sigma_2 \right] \mathbf{a},
\]

(II.7)

where \( N \) is the number of magnetic ions per unit volume.

To determine the phase boundaries, we note that in the P phase \( \hat{L} = 0 \) and thus \( \sigma_1 = \sigma_2 \) while in the AF phase \( \hat{L} \neq 0 \) so that \( \sigma_1 \neq \sigma_2 \). At \( H = 0 \), the transition between these two types of behavior occurs at the Néel temperature \( T_N \) given by

\[
T_N = \frac{2z|J|S(S+1)}{3k}
\]

(II.8)

Rewriting Eqs. (II.5) and (II.6) in terms of the reduced variables

\[
\tau \equiv \frac{T}{T_N}
\]

(II.9)
and

\[ h = \frac{g_\mu_B H}{2\pi |J| S}, \quad (II.10) \]

then

\[ \sigma_1(h, \tau) = B_S \left[ \frac{3S}{S+1} \left( \frac{h-\sigma_2}{\tau} \right) \right] \quad (II.11) \]

\[ \sigma_2(h, \tau) = B_S \left[ \frac{3S}{S+1} \left( \frac{h-\sigma_1}{\tau} \right) \right] . \quad (II.12) \]

The results of numerical solutions of these equations for \( S=\frac{1}{2} \) are shown in Figs. (II.2-4). Fig. (II.2) shows the reduced sublattice magnetizations \( \sigma_1 \) and \( \sigma_2 \) as a function of temperature at zero field. Figs. (II.3) and (II.4) show examples of curves calculated to determine a point on the AF-P phase boundary. In Fig. (II.3), \( h \) is kept fixed (at \( h=0.1 \)) while \( \tau \) is varied to find the transition. In Fig. (II.4) is held constant (at \( \tau=0.9975 \)) while \( h \) is varied. In either case, the AF-P transition is at the point where \( \sigma_1 \) becomes equal to \( \sigma_2 \) (i.e., \( \mathcal{L} \) becomes equal to zero). In both figures, this point is \( (h=0.1, \tau=0.9975) \).

Close to \( T=T_N \), an analytic solution for the AF-P phase boundary can be obtained by expanding the Brillouin function in Eqs. (II.11) and (II.12) for small argument. This gives

\[ \frac{T_N-T}{T_N} = 1-\tau = \frac{9}{40} \frac{(2S^2+2S+1)}{(S+1)^2} h^2 + O(h^4) \]

\[ = \frac{1}{4} h^2 + O(h^4) \quad \text{for} \quad S=\frac{1}{2} . \quad (II.13) \]
MFA $S=1/2$

$h=0$

Fig. (II.2). The spontaneous reduced sublattice magnetizations calculated according to the MFA at zero magnetic field.
Fig. (II.3). The reduced sublattice magnetizations in an MFA antiferromagnet in the vicinity of the Néel temperature (\( T = 1 \)) at zero magnetic field (\( h = 0 \)) and at a small magnetic field (\( h = 0.1 \)). At the AF-P phase boundary the two sublattice magnetizations become equal.
Fig. (II.4). The $H$-dependence of the reduced sublattice magnetizations in a MFA antiferromagnet as $H$ is increased through the AF-P phase transition.
**AF-SF Transition**

The AF-SF transition (spin-flop transition) is a first order transition. In the AF phase, the spins are oriented along the easy axis. As the magnetic field is raised, an abrupt reorientation to the SF configuration takes place. The spins now lie (for exchange much larger than anisotropy) almost perpendicular to the easy axis. The order parameter switches directions from $\hat{L}\parallel \hat{n}$ in the AF phase to $\hat{L}\perp \hat{n}$ in the SF phase. A standard formula for the spin-flop transition field $H_{SF}$ is

$$H_{SF} = \left( \frac{2K'}{\chi_{||} - \chi_{\perp}} \right)^{\frac{1}{2}},$$

where $K'$ is the anisotropy energy per unit volume and $\chi_{||}$ and $\chi_{\perp}$ are the (low field) susceptibilities per unit volume for $\hat{n}$ parallel and perpendicular to the easy axis, respectively.

This formula may be derived by considering the thermodynamic potential $\phi(T,P,H)$, analogous to the Gibbs free energy $G(T,P)$ for non-magnetic systems. This function is, in general, different for the AF and SF phases since the spin orientations are very different. The stable configuration, for given $T$ and $H$, is that which minimizes $\phi$.

Consider a 1 cm$^3$ sample at $H=0$ and $T<T_b$, and imagine that the SF phase (with $\hat{L}\perp \hat{n}$) could exist at $H=0$. In both the AF and SF configurations, there are two sublattices of spins oriented antiparallel to each other. In the AF phase, the
spins lie along the easy axis while in the SF phase, they are perpendicular to it. We define $K' = \Delta \phi(T,P) = \phi_{SF}(T,P,H=0) - \phi_{AF}(T,P,H=0)$, the difference of the free energy for the two configurations. (Notice, for an anisotropy of the form $-K_i S_i^2$, then $K' = \bar{K} S_i^2 / v$ where $v$ is the volume per magnetic ion.) The AF phase is stable (at $H=0$) when $K'>0$.

For either phase, we may calculate $\phi(T,P,H)$ from

$$d\phi = -\Omega dT + V dP - M dH,$$ \hspace{1cm} (II.15)

where $\Omega$, $V$, $M$ are the entropy, volume, and magnetization for that phase respectively. For fixed $T$ and $P$, this equation may be integrated to give

$$\phi_{AF}(H) = -\int_0^H M_{AF}(H') dH',$$ \hspace{1cm} (II.16)

where we have chosen the zero of energy $\phi_{AF}(T,P,H=0)=0$. When $\hat{H} \parallel \hat{a}$, and assuming that the susceptibility $\chi_{\parallel}$ measured with $\hat{H} \parallel \hat{a}$ is independent of $\hat{H}$, this gives

$$\phi_{AF}(H) = -\frac{1}{2} \chi_{\parallel} H^2.$$ \hspace{1cm} (II.17)

The SF configuration has

$$\phi_{SF}(H) - \phi_{SF}(H=0) = -\int_0^H M_{SF}(H') dH',$$ \hspace{1cm} (II.18)

or, for our choice of zero of $\phi(T,P,H)$, and if the susceptibility $\chi_{SF}$ is constant
\[ \phi_{SF}(H) = K' - \int_0^H M_{SF}(H')dH' = K' - \frac{1}{2} \chi_{SF} H^2 \quad (II.19) \]

\( \chi_{SF} \) cannot be measured below \( H_{SF} \), but when the anisotropy energy is small compared with the exchange energy, \( \chi_{SF} \) is nearly equal to \( \chi_\perp \), the low-field susceptibility measured with \( \hat{H} \parallel n \). (Both \( \chi_{SF} \) and \( \chi_\perp \) are for a configuration with \( \hat{L} \parallel \hat{H} \).) For \( T < T_N \), \( \chi_\perp \gg \chi_{ii} \) (see Fig. (II.5) which shows \( \chi_{ii} \) and \( \chi_\perp \) predicted using the MFA) so that \( \phi_{SF}(H) \) decreases with \( H \) faster than \( \phi_{AF}(H) \). Fig. (II.6) sketches the \( H \)-dependence of \( \phi_{AF}(H) \) and \( \phi_{SF}(H) \). The AF-SF transition will occur when \( \phi_{AF} = \phi_{SF} \). Using Eqs. (II.17) and (II.19), one obtains the formula in Eq. (II.14).

**SF-P Transition**

In the SF phase, the two sublattice magnetizations form equal angles \( \delta \) with the plane perpendicular to \( \hat{H} \), as sketched in Fig. (II.7). When the anisotropy is negligible, Eqs. (II.3) and (II.4) govern the system. In particular,

\[ \hat{H}_{eff}^{(1)} = \frac{2Jz}{\mu_B} \langle \hat{S}_z \rangle + \hat{H} \quad (II.20) \]

and

\[ |\langle \hat{S}_1 \rangle| = S B_S \left( \frac{\mu_B S}{kT} \left| H_{eff}^{(1)} \right| \right) \quad (II.21) \]

From the geometry (shown in Fig. (II.7)) it follows that
Fig. (II.5). The susceptibility $\chi = (d\sigma/dh)_{h=0}$ for a MFA antiferromagnet. Two curves are shown for magnetic field directed either parallel or perpendicular to the easy axis.
Fig. (II.6). The free energies for the AF and SF configurations in the presence of magnetic field. The spin-flop transition occurs at the field $H_{SF}$ where the curves cross.
\[ |\hat{H}_{\text{eff}}^{(1)}| = \frac{2Jz}{g\mu_B} |\langle \hat{S}_z \rangle| = \frac{2Jz}{g\mu_B} |\langle \hat{S}_z \rangle| = |H_{\text{eff}}^{(2)}| \quad \text{(II.22)} \]

and

\[ \sin \delta = \frac{H/2}{|H_{\text{eff}}^{(1)}|} = \frac{g\mu_B H}{4z|J||\langle \hat{S}_z \rangle|} \quad \text{(II.23)} \]

Substituting Eq. (II.22) into Eq. (II.21) one obtains a self-consistent equation for $|\langle \hat{S}_z \rangle|$. This equation does not contain $H$. Therefore, at a fixed $T$, the magnitude of the sublattice magnetization $|\langle \hat{S}_z \rangle|$ is independent of $H$ and is fixed (at the $H=0$ value, for example). A similar statement applies to $|\langle \hat{S}_z \rangle| = |\langle \hat{S}_z \rangle|$.

The SF-P phase transition occurs when $\sin \delta = 1$ (i.e., $\hat{M}_1$ and $\hat{M}_2$ become parallel so that $L$ becomes zero). The phase boundary is therefore given by

\[ H_{\text{SF-P}} = \frac{4z|J|}{g\mu_B} |\langle \hat{S}_z \rangle| \quad \text{(II.24)} \]

From a (self-consistent) solution for $|\langle \hat{S}_z \rangle|$ at $H=0$, the phase boundary may then be drawn. The analytic solution for the phase boundary near $T=T_N$, obtained by expanding the Brillouin function, is

\[ \frac{T_N - T}{T_N} = \frac{3}{40} \frac{(2S^2 + 2S + 1)}{(S+1)^2} h^2 + 0(h^4) \quad \text{(II.25)} \]

\[ = \frac{1}{12} h^2 + 0(h^4) \quad \text{for } S=\frac{1}{2} \]
Fig. (II.7). The equilibrium orientations of the sublattice magnetizations $\langle S_1 \rangle$ and $\langle S_2 \rangle$ in the SF phase. Also shown are various fields which act on sublattice $\#1$. 
where $h$ is the reduced field defined in Eq. (II.10).

This treatment must be modified if the anisotropy is non-zero. To lowest order, the effect of the anisotropy is to replace $T_N$ in Eq. (II.25) by $T_N^*$, where $T_N^* = T_N \left[ 1 - \frac{1}{2} \frac{H_A}{H_E} \right]$, and $H_A$, $H_E$ are the anisotropy and exchange fields at $T=0$, respectively.

Spin-Flop Bicritical Point

Under the MFA, the three phase boundaries in the $H$-$T$ plane (AF-P, SF-P, and AF-SF) of the uniaxial antiferromagnet with $\hat{H} \parallel \hat{n}$ meet at a point, which has been called the triple point in the past. However, there are differences between the usual definition of a triple point (as in $H_2O$ for example) and this point. In the uniaxial antiferromagnet, the three phases become indistinguishable at this point, while at a usual triple point the three phases remain distinct (the solid, liquid, and vapor phases in $H_2O$ for example).

Recently, theoretical interest has focused on the nature of this point and the behavior of physical qualities near it [3, 4]. In the terminology of critical phenomena, this point is currently known as the spin-flop bicritical point ($T_b, H_b$). At a bicritical point, two distinctly ordered phases (the AF and SF phases in this case) become identical to the totally unordered phase ($P$ here).

Of interest to the experiments reported here are the predictions of recent theories for the shape of the phase boundaries in the vicinity of the bicritical point. The three
phase boundaries are predicted to meet tangentially, with the ordered-disordered boundaries (AF-P and SF-P) curving inwards (towards lower T) to meet the ordered-ordered boundary (AF-SF) at the bicritical point. (See Fig. (11.8), for example.)

The scaling theory introduced to explain the behavior near \((T_b, H_b)\) focuses on the singular part of the free energy \(F_{\text{sing}}(T, \hat{H}^+, H)\). Here \(\hat{H}^+\) is the staggered magnetic field which acts like a magnetic field but alternates in sign from one sublattice to the other. \(\hat{H}^+\) contains the ordering fields for the AF and SF configurations. The component of \(\hat{H}^+\) along \(\hat{n}\), \(\hat{H}^+_{||}\), tends to induce the AF phase ordering while the component perpendicular to \(\hat{n}\), \(\hat{H}^+_{\perp}\), favors the formation of the SF phase. Most real antiferromagnets will have \(\hat{H}^+=0\), but the response to \(\hat{H}^+\) can be probed with neutron scattering.

The scaling hypothesis for the singular part of the free energy is that

\[
F_{\text{sing}}(T, \hat{H}^+, H) = \hat{t}^{2-\alpha} \cdot Y \left[ \frac{\hat{H}^+_{||}}{\hat{t}^{\Delta_{||}}}, \frac{\hat{H}^+_{\perp}}{\hat{t}^{\Delta_{\perp}}}, \frac{\hat{g}}{\hat{t}^\phi} \right],
\]

where \(\hat{t}\) and \(\hat{g}\) are two scaling variables which vanish at the bicritical point and measure deviations from this point along suitably chosen axes (in the \(H^2-T\) plane). The critical exponents are \(\Delta_{||}, \Delta_{\perp}, \alpha,\) and \(\phi\). The dependence of \(F_{\text{sing}}\) upon \(\hat{t}\) has thus been eliminated by a suitable scaling of \(F_{\text{sing}}\) and the real and staggered magnetic fields \(\hat{H}|| \hat{n}\) and \(\hat{H}^+\). Such a scaling
Fig. (II.8). The phase boundaries in the vicinity of the bicritical point according to either a) the MFA or b) the modern bicritical theory.
is justified by renormalization group arguments, and calculations by renormalization group methods give estimates of the parameters which enter (such as $\phi$ and choices of scaling axis).

Predictions for the location of the phase boundaries in the $H^2$-$T$ plane near the bicritical point are

\begin{align*}
(SF-P) \quad & \frac{\tilde{g}_C}{T^\phi} = \omega_\perp \quad \text{(II.27)} \\
(AF-P) \quad & \frac{\tilde{g}_C}{T^\phi} = -\omega_\parallel \quad \text{(II.28)}
\end{align*}

where $\omega_\parallel$ and $\omega_\perp$ are constants. We define $Q=w_\perp/w_\parallel$.

In terms of the reduced temperature $t=(T-T_b)/T_b$ and the magnetic field deviation $g=H^2-H_b^2$, the $\tilde{g}$ variable is chosen to measure deviations from the spin-flop (AF-SF) phase transition line (for $T<T_b$) or its continuation (for $T>T_b$).

\[ \tilde{g} = g - pt \quad \text{(II.29)} \]

where

\[ p = T_b \left( \frac{dH^2_{SF}}{dT} \right) \bigg|_{T=T_b} . \]

The second (linear) scaling variable is chosen to be

\[ \tilde{t} = t + qg \quad \text{(II.30)} \]

where $q$ is some constant.
Renormalization group calculations provide estimates of $\phi$, $Q$, and $q$. These estimates depend on $n$, the number of spin components exhibiting divergent bicritical fluctuations. ($n=3$ for a uniaxial system and $n=2$ for an orthorhombic case.) The predicted values are

$$\phi(n=3) \approx 1.25 \quad \phi(n=2) \approx 1.18$$

$$Q(n=3) \approx 2.51 \quad Q(n=2) = 1$$

and

$$q(n) = \frac{n+2}{3n} q_1 \quad q_1 = \frac{1}{T_b} \left[ \frac{dT_c^{||}}{dH^2} \right]_{H=0}$$

Here, $q_1$ is obtained from the initial slope of the AF-P phase boundary $T_c^{||}(H^2)$ in the $H^2-T$ plane.

Fig. (II.8) contrasts the phase boundaries near $T_b$ as predicted by the MFA and by the Bicritical scaling theory.

Thus, the shape of the phase boundaries (AF-P, SF-P) in the vicinity of the bicritical point are determined by seven parameters ($T_b$, $H_b$, $p$, $q$, $Q$, $\omega_{||}$, and $\phi$) of which three ($\phi$, $Q$, and $q$) may be estimated from the theory and two ($H_b$ and $p$) may be determined experimentally from the spin-flop transition line. The remained two parameters ($T_b$ and $\omega_{||}$) must be determined from fits of the AF-P and SF-P lines in the vicinity of $T_b$ to the theory (for example, by some least squares fitting approach). The fitting procedure may also allow some (or all) of the theoretically estimated parameters to vary as well.
The latter fits can be used to test the theory, i.e., to see whether the parameters obtained from the fits agree with the predicted values.

**Magnetostriuctive Effects at Phase Transitions**

Across a first order boundary, the free energy \( \Phi(T,P,H) \) is continuous but its first order derivatives are discontinuous. Thus, the entropy \( Q = -\partial \Phi / \partial T \), the total magnetic moment \( I = -\partial \Phi / \partial H \), and the sample volume \( V = \partial \Phi / \partial P \) exhibit discontinuous changes as the phase boundary is crossed. The (first-order) AF-SF transition is thus expected to be accompanied by discontinuous changes in sample volume.

At the spin-flop transition, there is a sudden reorientation of the magnetic moments and therefore a drastic change in the anisotropy energy. (There is also some change in the exchange energy.) The discontinuous change \( \Delta V \) in volume at \( H_{SF} \) then arises from the strain dependence of both the anisotropy and the exchange energies.

The change in volume is related to the derivative of the spin-flop field with respect to pressure by an expression analogous to the Clausius-Clapeyron equation [5]. Since \( \phi_{SF} = \phi_{AF} \) at the AF-SF boundary, it follows that

\[
-\Omega_{SF}dT - I_{SF}dH + V_{SF}dP = -\Omega_{AF}dT - I_{AF}dH + V_{AF}dP
\]

along the surface separating the AF and SF phases in the T-H-P space. Thus, keeping \( T \) fixed,
\[ \Delta V \equiv (V_{SF} - V_{AF}) = (I_{SF} - I_{AF}) \left( \frac{\partial H_{SF}}{\partial P} \right)_T. \]  

(II.33)

Dividing by \( V \), we get

\[ \frac{\Delta V}{V} = (M_{SF} - M_{AF}) \left( \frac{\partial H_{SF}}{\partial P} \right)_T. \]  

(II.34)

An analogous treatment for the discontinuous change \( \Delta \lambda \) in the length of the sample along a particular direction gives

\[ \frac{\Delta \lambda}{\lambda} = (M_{SF} - M_{AF}) \left( \frac{\partial H_{SF}}{\partial P} \right)_T, \]  

(II.35)

where \( P_u \) is a uniaxial pressure along \( \lambda \).

In the Ehrenfest theory of second order phase transitions, such transitions are accompanied by discontinuities in the second derivatives of the thermodynamic potential \( \phi \) (but the first order derivatives, as well as \( \phi \) itself, are continuous). Therefore, in that theory, the AF-P and SF-P transitions should be accompanied by discontinuities in \( \partial V/\partial H = \partial^2 \phi / \partial P \partial H \) and \( \partial V/\partial T = \partial^2 \phi / \partial P \partial T \). However, it is well known that many second order transitions (including the ones involved here) do not follow the Ehrenfest theory. Instead, the second order derivatives of the thermodynamic potential exhibit \( \lambda \)-singularities (as opposed to discontinuities) at the second order phase transitions. Such \( \lambda \)-singularities arise from short-range order effects. The MFA neglects these short-range order effects and it predicts discontinuities in \( \partial V/\partial H \).
and $\partial V/\partial T$, in agreement with Ehrenfest theory. More exact theories are expected to lead to $\lambda$-anomalies.

Near a second order transition, no discontinuous changes in either the anisotropy or the exchange energies take place. If the exchange energy is much larger than the anisotropy energy, the dominant magnetostrictive effects are expected to be due to the strain dependence of the exchange energy. As we shall see later, the strain dependence of the exchange energy leads to a volume magnetostriction. When $H$ or $T$ is changed, a change in volume $\Delta V$ occurs, the change being (approximately) proportional to the change in the nearest-neighbor two-spin correlation function $\eta(H,T)=\langle \hat{S}_i \cdot \hat{S}_j \rangle / S^2$ where $i$ and $j$ are nearest neighbors.

According to the MFA, $\eta(H,T)=\sigma_1(H,T)\sigma_2(H,T)$ in the uniaxial antiferromagnet. Fig. (II.9) shows the results of numerical evaluations of $\eta(h,T)$ using the MFA for a fixed temperature ($\tau=0.9975$) as a function of the reduced magnetic field. A change in slope of about 75% marks the position of the AF-P transition (at $h=0.1$). The magnetostriction should be approximately proportional to this curve. For comparison, Fig. (II.10) shows the total reduced magnetization $\sigma=(\sigma_1+\sigma_2)/2$. The change in slope which marks the transition is much less dramatic (only about 0.7%).

These calculations exemplify why magnetostriction measurements compare favorably with other techniques as a tool for determining phase transitions in antiferromagnets.
Fig. (II.9). The results of a hypothetical experiment to determine a point on the AF-P phase boundary by measuring the two-spin correlation function versus magnetic field at fixed $\tau=T/T_N$. The phase transition is at $h=0.1$. 

MFA $S=1/2$

$\gamma=0.9975$
Fig. (II.10). The results of a hypothetical experiment to determine a point on the AF-P phase boundary by measuring the magnetization versus $h$ at fixed $\tau=T/T_N=0.9975$. The phase transition at $h=0.1$ is accompanied by a change in slope of about $0.7\%$. 
REFERENCES


CHAPTER III

EXPERIMENTAL PROCEDURE

Apparatus

The linear magnetostriction and thermal expansion were measured by a capacitive technique using an apparatus similar to that described by White\(^1\) but modified\(^2\) to allow measurements on insulating samples to be performed.

One of the sample holders is sketched in Fig. (III.1a). A spring-loaded conducting plate (copper or brass) pushed the sample against a shim slug which, in turn, pushed against the frame of the capacitance cell. This frame also supported a fixed conducting plate a short distance (typically 0.15 mm) from the spring-loaded plate. All the surfaces within the measurement cell were nominally parallel. (The sample, slug, and spring-loaded plate had lapped parallel surfaces.)

As the sample expanded (or contracted), the gap between the spring-loaded and fixed plate varied. The change in the gap led to a change in the capacitance between the two plates, which was measured electrically, as discussed later.

Provision was made for the mounting of (resistance) thermometers on the measurement cell. The cell was suspended from a beryllium-copper rod and was enclosed in a copper can filled with a helium exchange gas. Outside the can, a bath of
Fig. (III.1). The sample holder is sketched in a and an idealized parallel plate capacitor is shown in b.
cryogenic liquid (liquid He, $H_2$, $N_2$, Ar, or one of the Freons 11, 12, 13, 14, or 216) was used to fix the temperature. By regulating the vapor pressure of the liquid, the temperature could be varied over a small range. The sample holder was installed in a Bitter-type solenoid magnet (in the Francis Bitter National Magnet Laboratory) so that the field was applied along the axis of the measurement cell.

Electrically, the holder comprised a three terminal guarded parallel plate capacitor (Fig. (III.1b)). (The parallel plate capacitor was formed by the fixed and spring-loaded plates. The guard was the frame.) By measuring the capacitance $C$ (typically 8 pf) of this parallel plate capacitor, the gap could be accurately determined. Any change $\Delta l$ in the length $l$ of the sample resulted in an equal but opposite change in the gap $g$. The change $\Delta C$ in capacitance resulting from a change $\Delta g$ in $g$ is

$$\frac{\Delta C}{C} = -\frac{\Delta g}{g} \quad (\text{III.1})$$

Since $\Delta g = -\Delta l$,

$$\frac{\Delta C}{C} = \frac{\Delta l}{g} = \left(\frac{\Delta l}{l}\right)\left(\frac{g}{l}\right) \quad (\text{III.2})$$

The great sensitivity of the capacitance technique for measuring $(\Delta l/l)$ stems from two factors: a) Capacitance can be readily measured with a precision of 1 part in $10^6$ using commercially available equipment; b) The ratio $(l/g)$ was
usually of order $10^{-2}$, so that $(\Delta C/C)$ was larger than $(\Delta l/l)$ by a "mechanical amplification factor" of order $10^{-2}$. The overall sensitivity is then on the order of one part in $10^{7}-10^{8}$.

Three different sample holders were used at different times. Two sample holders, essentially as in Fig. (III.1), allowed for the measurement of longitudinal $(\hat{z}||\vec{H})$ effects. One, built of brass, was used for magnetostriction measurements at fixed temperature. (Eddy-current heating caused by a change in $H$ is smaller in brass than in copper.) The other, built of copper, was used for phase boundary determination when $H$ was kept fixed and $T$ was swept. (The higher thermal conductivity of the copper rig reduced thermal gradients which existed in the holder when the temperature was swept.) The third sample holder, made of brass, was used to measure the transverse $(\hat{z}\perp\vec{H})$ magnetostriction. In this rig, $\vec{H}$ was parallel to the planes of the capacitor cell.

**Magnetostriction Measurement**

The capacitance was measured with a transformer ratio arm bridge (General Radio, type 1615A) driven with a $\sim$10 volt rms AC signal source at a frequency between 400 Hz and 1 kHz. A lockin amplifier was used as a null detector. Changes in capacitance could be measured either by rebalancing the bridge or by calibrating the lockin amplifier's output voltage (deviation from null) against bridge imbalance. The latter technique was usually used.
All the experiments consisted in looking at the small changes in sample length (and hence capacitance) that resulted from a change in either the magnetic field or the temperature. When the temperature was held fixed, the response of the sample to magnetic field, i.e., magnetostriction, was determined. When the field was held fixed and the temperature changed, the thermal expansion (in the presence of magnetic field) was being measured. In the latter case, there was a background arising from the thermal expansion of the frame of the capacitance cell. However, since we were interested only in the anomalies of the thermal expansion near phase transitions, this smooth background was not too important.

Changes in capacitance down to about $10^{-5}$ pf could be measured. This limiting resolution was largely due to random temperature fluctuations of $\pm 0.01$ K or less, giving rise to spurious signals. With typical sample sizes ($L/gC\omega l$), changes in sample length down to about $\Delta L/L \sim 1 \times 10^{-7}$ could be measured.

A few comments concerning the electrical properties of the capacitance cell are in order. A guarded parallel plate capacitor (as sketched in Fig. (III.1b)) is used with the electrode (1) and the guard (3) at the same electrical potential. If the guard-ring width w were zero, the capacitance between electrodes (1) and (2) would be that of an ideal parallel plate capacitor, namely,

$$C_{\text{ideal}} = \frac{\varepsilon A}{4\pi g} \text{ (esu)} \quad (\text{III.3})$$
Here, \( A = \pi r^2 \) is the area of electrode (1), \( g \) is the separation between the plates, and \( \varepsilon \) is the dielectric constant of the medium between the plates. The gas medium in the sample holder was helium at a low pressure, so we make take \( \varepsilon = 1 \).

(Even at 1 atm., the dielectric constant of He is \( \varepsilon = 1.00007 \) at 273 K\(^3\).) This expression must be corrected for a non-zero \( w \), the small correction being\(^{(1)}\)

\[
\frac{C}{C_{\text{ideal}}} = 1 + \frac{gw}{r(g+0.22w)} \left( 1 + \frac{w}{2r} \right). \tag{III.4}
\]

This provided a calibration between the measured capacitance and the gap \( g \) since the geometry (i.e., \( r \) and \( w \)) was known. More germane to the present experiments, it provided the connection between \( \Delta C/C \) and \( \Delta l/l \) which was accurate even for the small changes being measured in these experiments.

**Accuracy of Magnetostriction Measurement**

A number of considerations affect the accuracy of the magnetostriction measurements. The calibration in Eqs. (III.3) and (III.4) depends on the accuracy of the measurement of \( r \) and \( w \) (but the \( C \) vs \( g \) or \( \Delta C \) vs \( \Delta g \) calibration could not be in error by more than 0.3%). Non-parallelism of the plates will cause errors (estimated as \( \leq 1\% \) even if the gap changed 20% from edge to edge) as will other changes in the geometry. The calibration of the measurement cell has been checked by using shim slugs of different length and measuring the capacitance in each
case. On the basis of the results, the calibration was expected to be good to better than 1%.

More serious errors can occur when measurements on a magnetic sample are attempted. Forces and torques on the sample can distort the geometry (e.g., tilt the spring-loaded plate) during the course of a measurement, leading to spurious changes in the capacitance not related to sample elongation. Such effects should be small if the magnetic field is uniform over the volume of the sample and if the magnetization of the sample is parallel to the magnetic field so that the torque is small. By moving the sample away from the nominal centre of the magnetic field or tilting the sample holder away from its position (nominally colinear with the magnetic field) and remeasuring the magnetostriction, the effects of any torques were found to be small in our experiments (typically ≤2% for a 2cm movement or a 2° tilt).

The magnetostriction measurements were slightly sensitive to how the sample was installed. Typically, the reproducibility was ±5% from the mean of a large number of runs of the same experiment.

The background of the capacitance cell for magnetostriction experiments has been checked by measuring the magnetostriction of a number of materials (glass, G10, phenolic) which were expected to have negligible magnetostriction. Typically, a maximum ΔC/C of about ±1×10⁻⁵ was
found at 120kOe. The backgrounds were fairly consistent and could be corrected for in the data.

An independent calibration of the rigs was done by measuring the magnetostriction of a poly-crystalline nickel sample at 77 K. The measured values (means of a number of repeats of the measurement) were less than ±5% away from the expected value\(^4\). A correction was applied to the data to reflect this calibration procedure.

**Temperature Measurements**

In most cases, the temperature was set by regulating the vapor pressure of a cryogenic liquid. \(T\) was usually measured using a calibrated resistance thermometer. Two types of experiments were performed. In the first type, the temperature was held fixed so that the response of the sample to magnetic field could be measured. The temperature was always measured at zero field in these experiments. In the other type of experiment, the magnetic field was held fixed and the temperature swept slowly. The resistance thermometers were then read in the presence of magnetic field and a correction for their magnetoresistance was applied.

The resistance of the thermometers was measured using a constant current source (operated at 100\(\mu\)A to 1mA typically, stable to a few parts in \(10^5\)) in series with a standard resistor and the resistive temperature sensor. The voltage across the standard and the sensor were measured using a
Keithley type 140 DC Amplifier in combination with a digital voltmeter.

In the Hydrogen temperature range (16-20 K) a Germanium Resistance Thermometer (Cryocal type CR2055H-1.5-100-GenAB #3412; with a resistance at 20 K of 167 ohms) was used. The calibration as supplied with the thermometer was checked by a comparison with temperatures estimated from the Hydrogen bath's vapor pressure. A maximum error of about 0.02 K in the measured T values is estimated.

At higher temperatures, a Platinum Resistance Thermometer (Rosemount Engineering type 137DP #2743) was used. The calibration was checked against an NBS traceable standard PRT and a maximum error of about ±0.01 K near 77 K and ±0.02 K near 290 K in the measurement of T is estimated. For its use in the investigation of the phase boundaries of MnF$_2$, the magnetoresistance of this thermometer was measured at several temperatures near 65 K and could be corrected for to an accuracy of ±0.015 K in high magnetic field. The magnetoresistance amounts to about +3.7% (1.18 K equivalent) at 120 kOe at 65 K and agrees well with previous measurements$^5$ on similar thermometers.

In the determination of the AF-P and SF-P phase boundaries of Cr$_2$O$_3$, a thermistor (manufactured by the Keystone Co.) was used. This thermistor was calibrated against the PRT and its magnetoresistance was measured and corrected for in the data. Maximum errors of ±0.02 K in the thermistor vs PRT
calibration and ±0.003 K in the magnetoresistance correction at high field could occur. The magnetoresistance amounts to -0.03% (+0.008 K equivalent) at 120 kOe at 309 K.

**Magnetic Field Measurement**

Most experiments were performed in high-homogeneity Bitter-type solenoid magnets, a maximum field of 140 kOe being obtained with a current of 22 kA. The field homogeneity (1x10^-5 in a 1 cm³ sphere near magnetic center) insured that magnetic forces due to gradients in H were negligible.

Measurements at low fields (up to 3 kOe) were also made in such Bitter solenoids, but with a 500 A current supply replacing the Laboratory's high current generators.

The magnets were calibrated using a type-J Newport magnetometer, allowing for field determinations with a maximum error of 0.25% under optimal conditions. (Generator offsets equivalent to 0.3 kOe can occur during the course of a run or from day to day. Corrections--especially at low fields--were applied when warranted by the experiment.)

**Phase Transition Determination**

To locate a phase transition, either the magnetic field was held fixed while the temperature was swept slowly, or the temperature was held fixed while the magnetic field was swept slowly.

The first-order (AF-SF) transition in Cr₂O₃ was investigated using the latter technique. An X-Y recorder was used
to trace out curves of the magnetostriction (as represented by the lockin amplifier output voltage) versus H. These curves could then be analyzed to determine the location of the phase transition and the magnitude of the jumps in crystal length which accompanied the transition.

The second-order phase transition (AF-P and SF-P in the uniaxial antiferromagnets, and the ferromagnetic to paramagnetic transition at H=0 in the ferromagnet EuS) are expected to exhibit \( \lambda \)-anomalies in the derivatives of sample length with respect to swept variable (H or T). By digitizing the lockin output voltage and the swept variable, the sweeps could be stored and analyzed by computer. Typically, a sampling rate of 30 points/minute and sweep rates of 0.01-0.1 K/min or 1-3 kOe/min were used. The derivatives \( \frac{dC}{dT} \) or \( \frac{dC}{dH} \) could then be found by least-squares fitting a polynomial of order 1-3 at every point of the digitized data using a small number (perhaps 10-50) of the neighboring points. The derivative of this polynomial could then be evaluated numerically at the center point. The resultant curves of derivative versus swept variable could then be examined to obtain the location of the phase transition. The choice of the type of fit used involved a tradeoff between inaccuracy in transition location due to rounding of the \( \lambda \)-anomalies by the fitting procedure versus inaccuracy in location due to noise in the curves. The error bars quoted include estimates of these
uncertainties found by examining different fitting procedures as applied to the same data.

Demagnetization Correction

In experiments on magnetic materials, it is important to distinguish between the external applied magnetic field \( \vec{H}_{\text{ext}} \), and the internal field \( \vec{H}_{\text{int}} \). It is \( \vec{H}_{\text{int}} \) which is to be identified as the field \( \vec{H} \) in the theoretical discussions in Chapters II and VI. For a uniform ellipsoid in a uniform magnetic field, the internal field is given by

\[
\vec{H}_{\text{int}} = \vec{H}_{\text{ext}} - N \vec{M}
\]  

(III.5)

where \( N \) is the demagnetizing factor and \( \vec{M} \) is the magnetization. For a non-ellipsoidal sample (such as the ones used in the present experiments) \( \vec{H}_{\text{int}} \) is not uniform inside the sample. An exact correction for the demagnetizing field is not possible in such a situation. Fortunately, the demagnetization corrections in both \( \text{Cr}_2\text{O}_3 \) and \( \text{MnF}_2 \) were small (<1%) so that a rough estimate of the correction was sufficient. In EuS, however, the demagnetization correction was important. The correction for EuS will be discussed later.
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CHAPTER IV

THE PHASE DIAGRAM OF \( \text{Cr}_2\text{O}_3 \) FOR \( \vec{H} \parallel \text{EASY-AXIS} \)

General Properties of \( \text{Cr}_2\text{O}_3 \)

\( \text{Cr}_2\text{O}_3 \) crystallizes in the corundum structure, with a rhombohedral unit cell \((a_0=5.350 \, \text{Å}, \alpha=55^\circ \, 9')\) containing two \( \text{Cr}_2\text{O}_3 \) molecules and hence four \( \text{Cr}^{3+} \) ions \((S=3/2, \, g=1.97 \, (1)\) at \( T=0 \, \text{K} \)). The \( \text{Cr}_2\text{O}_3 \) molecules are in a body-centered rhombohedral arrangement with the \( \text{Cr}^{3+} \) ions located on the body diagonal (the trigonal or c axis) but every other molecule is rotated \( 60^\circ \) about the c axis. The crystal structure is sketched in Fig. (IV.1).

\( \text{Cr}_2\text{O}_3 \) is an antiferromagnet, with a Néel temperature \( T_N=307 \, \text{K} \). Below \( T_N \), the spins order parallel or antiparallel to the c axis, alternating in direction from one ion to the next along the trigonal axis.\((2, \, 3)\)

There is a strong antiferromagnetic exchange coupling between the two \( \text{Cr}^{3+} \) ions within a molecule (they are nearest neighbors, \( z_1=1 \)) and a weaker antiferromagnetic exchange with each of the \( z_2=3 \) next-nearest neighbors (which are ions in another molecule). Fig. (IV.2) shows the arrangement of the spins in a plane containing the trigonal axis, with four exchange bonds indicated. The exchange constants are\((4)\)

\( J_1/k=-86 \, \text{K}, \, J_2/k=-38 \, \text{K}, \, J_3/k=-6 \, \text{K}, \, J_4/k=-2 \, \text{K} \) with uncertainties
Fig. (IV.1). The rhombohedral unit cell of $\text{Cr}_2\text{O}_3$. 
Fig. (IV.2). The spin ordering of the Cr\(^{3+}\) magnetic ions of Cr\(_2\)O\(_3\) in a plane containing the trigonal axis.
of ±6 K. These are estimated from neutron scattering and antiferromagnetic resonance data.

The anisotropy is uniaxial with easy-axis being the trigonal and anisotropy constant \( \bar{K}/k = 0.015 \) K at \( T = 0 \). The anisotropy field for this value of \( \bar{K} \) is then \( H_A = 700 \) Oe = \( (2.8 \times 10^{-4}) H_E \), where \( H_E \) is the exchange field.

Samples and Sample Preparation

Two single crystal samples were used. Each was oriented using x-rays and cut to have a pair of c faces. These c faces were then lapped flat and parallel to each other. It was estimated that during the experiments the magnetic field was applied within 2° of the c-axis, for both samples.

Sample #1 was 3.3 mm in length along the c-axis and sample #2 was 3.6 mm. The mechanical amplification factor obtained with the sample holders was then \( \sqrt{20} \) -- i.e., a fractional change in length \( \Delta l/l \) of the sample caused a change \( \Delta C/C \approx 20 \times (\Delta l/l) \) in the capacitance. Changes in \( (\Delta l/l) \) down to about \( 5 \times 10^{-8} \) could then be detected.

The small susceptibility of \( Cr_2O_3 \) \(^{(1)} \) assured that the correction for the demagnetizing field was less than 0.1% of \( H \) and hence it was ignored in the data analysis.

Néel Temperature

The Néel temperature was determined from the lambda anomaly at \( T_N \) in the thermal expansion coefficient, measured along the c-axis, \( \alpha_c = \frac{1}{C} \frac{dC}{dT} \). Fig. (IV.3) shows a sweep of C
Fig. (IV.3). A sweep of $\ell(\text{H}=0,T)$ versus $T$ across the AF-P phase transition.
versus $T$ at $H=0$ where $\lambda$ was measured along the $c$-axis. (The curve is for sample #1.) $T$ was measured using the calibrated thermistor. This sweep, over a range of about $0.6\,\text{K}$, took about 15 minutes. It was recorded digitally and consists of about 400 pairs of $(C,T)$ values.

Fig. (IV.4) shows the result of computer analysis of the data in Fig. (IV.3) in order to determine the slope $dC/dT$ as a function of $T$. A $\lambda$-like dip in $dC/dT$ (and hence, a $\lambda$-like dip in $\alpha_c$) at the Néel temperature is evident. To obtain this curve, a first order polynomial was fit to 35 points centered around every digitized point. The derivative of this polynomial was then evaluated numerically at the center point. Thus, this procedure used a width of $\sim 0.05\,\text{K}$ in $T$ to obtain the slope. Some rounding of the $\lambda$-anomaly due to this procedure is hence expected, but the method used to choose a value of $T_N$ minimized the effect of this rounding. The method used to choose $T_N$ is illustrated in Fig. (IV.4). The $dC/dT$ curve on each side of $T_N$ was extrapolated. The value of $T$ where the lines met was chosen to be $T_N$. $T_N$ could thus be located within a range of about $0.02\,\text{K}$ for sample #1. (Sample #2 had somewhat less sharp $\lambda$-dips and uncertainties where $\sim 0.04\,\text{K}$.) Differences in temperature $(T-T_N)$ could then be measured to an accuracy of $0.02-0.03\,\text{K}$ for sample #1 and $\sim 0.06\,\text{K}$ for sample #2. Absolute determinations of the temperature also took into account the uncertainties in
Fig. (IV.4). The computer-evaluated derivative $\frac{d\xi}{dT}(H=0,T)$ versus $T$. The AF-P transition is accompanied by a $\frac{d^2}{dT^2}$ $\lambda$-like anomaly in $d\xi/dT$ which may be used to determine $T_N$, as indicated in the figure.
thermometer calibration, but the calibration had only a minimal effect on the accuracy of \((T-T_N)\) measurements.

The Néel temperatures as determined from this procedure are \(T_N = 307.3 \pm 0.1\) K for sample #1 and \(T_N = 307.5 \pm 0.1\) K for sample #2. These numbers are averages of a number of \(T_N\) determinations.

The thermal expansion was also measured along the binary direction (2-fold axis) at \(H=0\). For this direction, a \(\lambda\)-like peak in the thermal expansion coefficient was found. The polarity of these observations (dip along the \(c\), peak along the binary) are consistent with x-ray data for the lattice parameter of \(\text{Cr}_2\text{O}_3\).\(^{(5)}\)

The boundaries between all three phases (AF, SF, and P) of \(\text{Cr}_2\text{O}_3\) were investigated in this study. The AF-P and SF-P transitions were studied by means of the anomalies in the thermal expansion in the presence of magnetic fields. The \(T_N\) determination is a typical experiment of this type. The AF-SF transition was studied by measuring the magnetostriction as the boundary was crossed.

**Spin-Flop Transition**

The spin-flop (AF-SF) transition in \(\text{Cr}_2\text{O}_3\) has been studied previously by a variety of techniques. These include measurements of the differential magnetization\(^{(6)}\), magneto-electric effect\(^{(7)}\), antiferromagnetic resonance and susceptibility\(^{(1)}\), ultrasonic attenuation\(^{(8)}\), and magnetostriction\(^{(9)}\).
The spin-flop transition is a first-order transition. Such a transition is characterized by discontinuous changes in the first-order derivatives of the free energy. In particular, a sample is expected to exhibit abrupt changes in its dimensions as the AF-SF boundary is crossed. Such behavior has been seen in the previous magnetostriction measurements.\(^{(9)}\) In those experiments, the jumps in the longitudinal and transverse magnetostrictions at the spin-flop transition were measured in pulsed magnetic fields but were confined to low temperatures (T<100 K).

We have extended the longitudinal magnetostriction measurements to cover a temperature range from 4 K to 307 K. This temperature range spans almost the entire AF-SF boundary.

For fixed T, the longitudinal magnetostriction versus H, \(H \parallel c\)-axis\( \parallel \hat{\ell} \), was traced out using an X-Y recorder. A typical trace is shown in Fig. (IV.5). Plotted is the fractional change in length, \(\Delta \ell / \ell = \ell (H) - \ell (0) / \ell (0)\), against H. As H was increased from zero, \(\ell (H)\) remained almost constant until the AF-SF boundary was neared. Then, as H scanned through \(H_{SF}(T)\), the sample elongated along the c-axis by an amount \(\delta \ell / \ell\). The width of the transition region, measured between the points where 10% and 90% of the total elongation occurred, was, at low temperatures (T<80 K), measured to be \(\sim 5\) kOe in sample #1 and \(\sim 6\) kOe in sample #2. The widths increased as T was raised towards \(T_{p}\), reaching maximum values of \(\sim 8\) kOe and \(\sim 10\) kOe in the two samples. Part of these widths may have been due to
Fig. (IV.5). The $H$-dependence of $\Delta l/l = [l(H) - l(0)]/l(0)$ at 77.8 K. A jump in length, $\delta l$, accompanies the spin-flop transition at $H_{sf}$. 

Cr$_2$O$_3$, H∥∥∥c

$T = 77.8$ K
small misalignments of each sample from the $\vec{H}||\vec{c}$ nominal configuration. Above the transition region, the sample length again remained almost constant, but at its new value. Traces of this sort were analyzed to determined $H_{SF}$ and $\delta l/l$ as functions of temperature.

$H_{SF}(T)$ was defined as the field at the midpoint of the elongation. The experimentally determined AF-SF phase boundary is plotted in Fig. (IV.6). The $H_{SF}(T)$ points in this figure are averages for the two samples. The values for sample #2 were higher than those of sample #1 by 1-2 kOe. $H_{SF}(T)$ increased monotonically from $H_{SF}(4.2 \text{ K})=59.3 \pm 1.5$ kOe to $H_{b} = H_{SF}(T_{b})=121.8 \pm 2$ kOe. These results agree with the previous measurements of the position of the AF-SF boundary.\(^6\)\(^9\)

The solid curve in Fig. (IV.6), along the AF-SF boundary, is calculated from Eq. (II.14), namely,

$$H_{SF}(T) = \left( \frac{2K'}{\chi_{\perp} - \chi_{||}} \right)^{\frac{1}{3}} \quad \text{(IV.1)}$$

Data for $K'/\chi_{\perp}$ and $(\chi_{\perp}/\chi_{||})$ as functions of temperature have been taken from ref. (1). The agreement with the experimental points is very good.

Fig. (IV.7) presents the measured values of $\delta l/l$ as a function of $T$. Again, averages for the two samples are plotted. The values for sample #2 were in general higher than those for sample #1 by 5-10%. At $T=4.2 \text{ K}$, $\delta l/l=(3.5 \pm 0.4) \times 10^{-5}$. \(6\)\(9\)
Fig. (IV.6). The AF-SF phase boundary as determined from the jumps in the magnetostriction. The solid curve is calculated from Eq. (IV.1). The broken curve indicates the position of the AF-P and SF-P phase boundaries.
Fig. (IV.7). The T-dependence of the jump in length $\delta l$ which accompanies the spin-flop transition.
This is similar to the previously reported value of $\delta l/l = 2.8 \times 10^{-5}$ at low temperatures.

The magnetic analog of the Clausius-Clapeyron equation relates $\delta l/l$ to the (uniaxial) pressure dependence of $H_{SF}$, namely Eq. (II.35),

$$\frac{\delta l}{l} = (M_{SF} - M_{AF}) \frac{\partial H_{SF}}{\partial P_u}$$  \hspace{1cm} (IV.2)

$$= H_{SF} (\chi_{\perp} - \chi_{\parallel}) \frac{\partial H_{SF}}{\partial P_u}.$$  \hspace{1cm} (IV.2)

Using the value $\left(\frac{\partial H_{SF}}{\partial P_u}\right) = 4.5 \text{ Oe/bar}^{(10)}$, and the magnetization data of ref. (1), Eq. (IV.2) predicts $\delta l/l = 3.0 \times 10^{-5}$ at 4.2 K, in reasonable agreement with our measured value.

**Bicritical Region**

We now turn to the other phase boundaries of $\text{Cr}_2\text{O}_3$---the AF-P and SF-P boundaries. Except for the measurement of $T_N$, there has been very little experimental work done on these boundaries. The AF-P and SF-P transitions are second-order transitions. They are accompanied by $\lambda$-like anomalies in the second-order derivatives of the free energy (the first-order derivatives and the free energy itself being continuous). In the present experiments, the thermal expansion coefficient, $\alpha_c$, was measured at fixed $H$ in the vicinity of the AF-P and SF-P boundaries. $\lambda$-like dips occurred when either the AF-P or the SF-P boundary was crossed. The position of these dips was
determined by following a procedure identical to the $T_N$ determination described above. Fig. (IV.8) contrasts the curves of $d\ell/dT$ obtained from the computer analysis of sweeps at three values of $H$. As is evident from the figure, the position of the $\lambda$-like dip changes as the magnetic field changes. The sweeps at $H=0$ and $H=113$ kOe determine points on the AF-P boundary. The sweep at $H=124$ kOe determines a point on the SF-P boundary.

Figs. (IV.9) and (IV.10) show the phase boundaries for sample #1 for $H<180$ kOe, plotted in the $H$-$T$ and $H^2$-$T$ planes, respectively. Errors in the experimental AF-P and SF-P transition points were estimated to be at most $\pm 0.5$ kOe in $H$ and $\pm 0.025$ K in $(T-T_N)$. The curves for the other sample are similar, except for slightly more scatter in the points, due mainly to the wider $\lambda$-anomalies for that sample.

We have presented in Chapter II two theories which attempt to predict these phase boundaries from the Heisenberg model for an antiferromagnet—the Mean Field Approximation and the bicritical theory due to Fisher, Nelson and Kosterlitz.\(^{11-13}\) According to the MFA, the AF-P and SF-P boundaries should be almost straight lines in the $H^2$-$T$ plane, with the slopes $(dH_{AF-P}/dT)$ and $(dH_{SF-P}/dT)$ both being negative and being in the ratio $\left(\frac{dH_{SF-P}}{dT}\right)/\left(\frac{dH_{AF-P}}{dT}\right)=3$ (see Eqs. (II.13) and (II.25)). Any non-linearities should be of order $h^2=\frac{\mu_B H}{2z |J| S}^2 \approx 5 \times 10^{-4}$ when $H \approx 100$ kOe for $\text{Cr}_2\text{O}_3$. Examining Fig. (IV.10), however, we see first that the AF-P boundary,
Fig. (IV.8). The T-dependence of \((d\chi/dT)_H\) at three different magnetic fields. \(\lambda\)-like anomalies in \((d\chi/dT)_H\) occur at both an AF-P transition \((H=0 \text{ and } H=113 \text{ kOe})\) and an SF-P transition \((H=124 \text{ kOe})\).
Fig. (IV.9). The AF-P and SF-P phase boundaries of Cr$_2$O$_3$ in the H-T plane for $\vec{H} \parallel c$-axis as determined from the $\lambda$-anomalies in the thermal expansion coefficient.
Fig. (IV.10). The AF-P and SF-P phase boundaries of Cr$_2$O$_3$ in the $H^2$-T plane for $\mathbf{H} \parallel c$-axis as determined from the $\lambda$-anomalies in the thermal expansion coefficient.
although fairly straight at low \( H \), "flattens out" as \( H \) approaches \( H_b \). At low values of \( H \), the slope of the AF-P line is \( (dH_{AF-P}^2/dT) = -(3.2 \pm 0.6) \times 10^9 \) Oe²/K. (This is an average for the two samples.) The MFA, however, predicts a value \(-1 \times 10^{11} \) Oe²/K. Thus, even for small \( H \), the experimental boundary curves inwards towards lower \( T \) much faster than the MFA would predict. Even worse, for \( H \) just above \( H_b \), the SF-P boundary curves outwards towards higher \( T \) as \( H \) increases, so that even the sign of \( (dH_{AF-P}^2/dT) \) is not correctly given by the MFA.

The bicritical theory, on the other hand, predicts just such behavior by the phase boundaries near \( T_b \).

To compare the AF-P and SF-P boundaries to the bicritical theory presented in Chapter II, a least-squares analysis was undertaken. The theory predicts the shape of the AF-P and SF-P phase boundaries near \((H_b, T_b)\) in terms of seven parameters. Some of these parameters may be determined without reference to these lines near \( T_b \). Table (IV.1a) lists the experimentally determined parameters. They are: a) \( q_1 \), the slope \(-T_b^{-2} \frac{dT}{dH} \) of the AF-P line at \( H=0 \); b) \( p \), the slope \(-T_b^{-2} \frac{dH^2}{dT} \) of the spin-flop (AF-SF) boundary in the \( H^2-T \) plane near \( T_b \); and c) \((H_{b0}, T_{b0})\), a point on the AF-SF line near \( T_b \).

The three parameters \( p \), \( H_{b0} \), and \( T_{b0} \) are used to fix the position of the AF-SF boundary near \( T_b \). The theory of Fisher, et al. approximates this boundary by a straight line in the
### TABLE (IV.1)

THE BICRITICAL POINT OF Cr$_2$O$_3$ FOR SAMPLE #1

a) Parameters taken from experiment:

\[
T_N = 307.3 \pm 0.1 \text{ K}
\]

\[
q_1 = \frac{1}{T_b} \left( \frac{dT_{c||}}{dH^2} \right)_{H=0} = (9.5 \pm 0.8) \times 10^{-14} \text{ Oe}^{-2}
\]

\[
p = T_b \left( \frac{dH^2_S}{dT} \right)_{T=T_b} = (2.9 \pm 0.3) \times 10^6 \text{ Oe}^2
\]

\[
[T_{b0} - T_N, H_{b0}] = (-0.485 \pm 0.03 \text{ K}, 120.0 \pm 0.5 \text{ kOe})
\]

b) Parameters obtained by least-squares fitting to experimental data. (Quantities in brackets are chosen by the fitting procedure.)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>1</th>
<th>2</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>type of fit</td>
<td>1/3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Q</td>
<td>2.51</td>
<td>2.51</td>
<td>2.51</td>
<td>2.51</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>$\phi$</td>
<td>1.25</td>
<td>1.25</td>
<td>(1.43)</td>
<td>1.18</td>
<td>1.18</td>
<td>(1.25)</td>
<td></td>
</tr>
<tr>
<td>$T_b - T_N$ (K)</td>
<td>(-0.476)</td>
<td>(-0.508)</td>
<td>(-0.485)</td>
<td>(-0.475)</td>
<td>(-0.493)</td>
<td>(-0.485)</td>
<td></td>
</tr>
<tr>
<td>$q$ ($10^{-15}$ Oe$^{-2}$)</td>
<td>(1.45)</td>
<td>5.25</td>
<td>(1.36)</td>
<td>(4.32)</td>
<td>6.30</td>
<td>(4.41)</td>
<td></td>
</tr>
<tr>
<td>$\omega_{</td>
<td></td>
<td>}$ ($10^{13}$ Oe$^2$)</td>
<td>(6.11)</td>
<td>(3.08)</td>
<td>(22.81)</td>
<td>(4.96)</td>
<td>(3.58)</td>
</tr>
<tr>
<td>RMS deviation (K)</td>
<td>(0.008)</td>
<td>(0.054)</td>
<td>(0.008)</td>
<td>(0.010)</td>
<td>(0.018)</td>
<td>(0.011)</td>
<td></td>
</tr>
</tbody>
</table>
H^2-T plane. In principle, (T_{b0}, H_{b0}) may be chosen to be any point on this straight line without affecting the results of the fitting procedure. In practice, (H_{b0}, T_{b0}) is chosen not only to be a point on the AF-SF line, but also to be an estimate of the actual bicritical point. The estimate is obtained by inspection from plots such as Fig. (IV.10).

The fitting procedure minimized the quantity

$$
\sum_i (T_i - T_{\text{fit}}(H_i))^2 G_i.
$$

Here, (T_i, H_i) is an experimental point on one of the AF-P or SF-P boundaries. T_{\text{fit}}(H) is the prediction of the bicritical theory for the phase boundaries, as given by Eqs. (II.27) and (II.28) with parameters chosen by the fitting procedure. The G_i are weights, chosen so that equal weight was given to points above and below H_b. If there were n_\parallel points on the lower (H<H_b) boundary and N_\perp points on the upper boundary (H>H_b), then the weights were chosen to be

$$
G_i = G_{\parallel} = \frac{n_\parallel}{n_\parallel + n_\perp}
$$

for data points on the lower boundary and

$$
G_i = G_{\perp} = \frac{n_\perp}{n_\parallel + n_\perp}
$$

for points on the upper boundary.

Three types of fit were attempted: 1) a fit in which T_b, \omega_\parallel, and q were allowed to vary. Q and \phi were taken from theory and (T_{b0}, H_{b0}) and p from experiment; 2) a fit in which only T_b and \omega_\parallel were allowed to vary---i.e., the same as fit #1 but with q taken from theory; and 3) a fit in which \phi, \omega_\parallel, and q were allowed to vary (T_b was held fixed at the value T_{b0}).

The type 2 fit took as much information about the parameters as possible from theory. Only \omega_\parallel (for which there is no estimate in the theory) and T_b (which, in these experiments,
can only be determined from the AF-P and SF-P boundaries in the bicritical region) were allowed to vary. The type 1 fit also allowed $q$ to vary. $q$ determines the position of the $t=0$ scaling axis in the $H^2$-$T$ plane. So, in effect, the type 1 fit chose an optimal scaling axis for the experimental data. The type 3 fit can be of use when detailed data near $T_b$ is available. In that case, the bicritical point can be determined by inspection, and the type 3 fit used to find an experimental estimate for the cross-over exponent $\phi$ for comparison with the theoretical value.

The theoretically predicted values for the parameters depend on the form of anisotropy that is assumed--i.e., on the value of $n$. Fits were performed for the case of $n=3$, which is appropriate for a purely uniaxial antiferromagnet (i.e., cylindrical symmetry), and for the case of $n=2$, which would be obtained if there was an anisotropy within the $c$-plane favoring certain orientations of the flopped-phase spins. By comparing fits which assume different values for $n$, it was then possible to decide what model for the anisotropy gave better fits to the data.

Table (IV.1b) presents the results of these fitting procedures applied to the experimental data on sample #1 for $H=100$ kOe. From an examination of the table, we make the following observations: 1) the rms errors in the fitted vs. experimental points suggest that for the type 2 fits, the $n=2$ case provides a better description of the data. All the type
1 and 3 fits (for both n=2 and n=3) produce about the same error—essentially the experimental scatter; 2) the values for \( q \) obtained from fits of type 1 and 3 are closer to the theoretical estimate in the case of n=2 than in the case of n=3; and 3) the variation in the fitted values of \( T_b \) and fitted for n=2 is less than for n=3.

One possible explanation of these observations is that we must assume n=2 to get the best fit between experiment and theory. This is equivalent to assuming that there is sufficient anisotropy within the c-plane that, at least for comparison with the bicritical theory, we cannot treat our \( \text{Cr}_2\text{O}_3 \) sample as being a pure uniaxial antiferromagnet (having a pure cylindrical symmetry). In any real crystal, there will always be some anisotropy within the c-plane. One measure of the effectiveness of any such in-plane anisotropy in determining a preferred orientation of the spin system is the so-called "in-plane spin-flop field." As an estimate, if we assume that the in-plane anisotropy chooses a set of preferred in-plane axes, then by a procedure similar to the calculation of the "usual" spin-flop field, we can write an analog to Eq. (II.14), namely,

\[
H_{\text{SF (in-plane)}} = \left[ \frac{2K' \text{ (in-plane)}}{\chi_\perp - \chi_\parallel} \right]^\frac{1}{2}
\]

(IV.3)

If we take \( K' \text{ (in-plane)} \) to be only 0.1% of the usual uniaxial anisotropy constant, then \( H_{\text{SF (in-plane)}} \approx 2 \text{ kOe at } T=0 \) and
$\approx 4$ kOe near $T_b$. Obviously, it does not require a large in-plane anisotropy to destroy the approximation of cylindrical symmetry.

The phase boundaries drawn in Figs (IV.9) and (IV.10) are those generated by the $n=2$, type 1 fit (with parameterization as given in Table (IV.lb)). Fig. (IV.11) contrasts this fit (in essence, the "best" fit) with the type 2 fits for $n=2$ and $n=3$. Notice that qualitatively the $n=2$ fit seems much superior.

Conclusions

All three phase boundaries in the $H$-$T$ plane of $\text{Cr}_2\text{O}_3$, in magnetic fields $H$, $\mathbf{H} \parallel c$, up to 180 kOe have been investigated in this study. The AF-SF transition exhibited jumps in the samples' dimensions as the boundary was crossed. The phase boundary, as determined by measuring the location of these jumps, was in good agreement with the previous experiments on the location of the boundary and in good agreement with the theoretical calculation of its position.

The AF-P and SF-P transitions exhibited $\lambda$-like anomalies in the thermal expansion coefficient, $\alpha_c$, measured at fixed $H$. The phase boundaries were determined by measuring the location of these anomalies. The phase boundaries so determined were in good qualitative agreement with the recent bicritical theory of Fisher, Nelson, and Kosterlitz. In contrast, the Mean Field Approximation gave a very poor
Fig. (IV.11). The AF-P and SF-P phase boundaries of \textit{Cr}_2\textit{O}_3 near \(T_b\) according to the bicritical theory, with parameters chosen by least-squares fits to the data for \(H>100\ \text{kOe}\). The solid curve represents the "best" fit (type 1, \(n=2\)). The broken curves are type 2 fits for \(n=3\) (cylindrical symmetry) and \(n=2\) (orthorhombic symmetry).
estimate of the position of the boundaries, particularly the SF-P boundary.

Quantitative comparisons of the experimental AF-P and SF-P boundaries and the predictions of the bicritical theory were performed by a least-squares fitting technique. The results of the analysis suggested that in order to obtain the best fit between experiment and theory, one had to assume \( n=2 \)--i.e., one had to assume that there was sufficient anisotropy within the c-plane to invalidate the modeling of \( \text{Cr}_2\text{O}_3 \) as a pure uniaxial antiferromagnet. Alternatively, one may retain the assumption \( n=3 \) (cylindrical symmetry), but then the theoretical estimate of \( q \) in terms of \( \left( \frac{dT_c''}{dH} \right)_{H=0} \) must be modified.
REFERENCES

CHAPTER V

THE PHASE BOUNDARIES OF MnF₂
NEAR THE BICRITICAL POINT

General Properties of MnF₂

MnF₂ has a rutile structure with the magnetic Mn²⁺ ions (g=2.00, S=5/2) arranged on a body-centered tetragonal lattice (with a=4.8734 Å and c=3.3099 Å). MnF₂ is an antiferromagnet with a Néel temperature $T_N=67.3$ K. In the ordered state, the material consists of two equivalent, interpenetrating sublattices. One sublattice is composed of the body-center ions and the other of the corner ions. Below $T_N$, at $H=0$, the two sublattice magnetizations are antiparallel to each other and directed along the c axis (the tetragonal axis, [001]).

The dominant exchange interaction of any Mn²⁺ ion is an antiferromagnetic interaction with $z_2=8$ Mn²⁺ ions on the other sublattice which are its next-nearest neighbors. (In a body-centered cubic material, the corner ions are nearest neighbors of the center ion. However, because the c/a ratio for MnF₂ is 0.68, the corner ions are next-nearest neighbors of the center ion.) There is also a weak ferromagnetic interaction between any ion and its $z_1=2$ nearest neighbors (which are ions on the same sublattice).
The magnetic anisotropy of \( \text{MnF}_2 \) is uniaxial, with the easy axis being the c axis. The S-state of the \( \text{Mn}^{++} \) ion couples only weakly to the crystal field and as a result, the anisotropy is largely due to the dipole-dipole interaction.\(^{(1)}\)

The exchange and anisotropy constants have been determined\(^{(2-4)}\) by combining measurements of the susceptibility, antiferromagnetic resonance, and neutron scattering (all at \( T < T_N \)) to give \( J_1/k = 0.32 \) K, \( J_2/k = -1.76 \) K, \( |J_3|/k < 0.05 \) K, and \( K/k = 0.212 \) K. \( J_1, J_2, \) and \( J_3 \) are the nearest, next-nearest, and third-nearest neighbor exchange constants. The anisotropy constant is \( K \) and is equivalent to an anisotropy field \( H_A = 7.9 \) kOe=0.0139 \( H_E \), where \( H_E = 5.6 \times 10^5 \) Oe is the exchange field.

Because of its simple crystal structure, simple magnetic structure, low anisotropy, and convenient \( T_N \), \( \text{MnF}_2 \) is one of the better studied antiferromagnets. As such, it is a "classical" material to do experiments on.

**Sample and Sample Preparation**

The \( \text{MnF}_2 \) sample used for these experiments was cut from a single crystal grown by Optovac. The sample was approximately cubical in shape. It had a pair of (001) faces lapped flat and parallel, with a length along the c-axis of about 4.8 mm. With a typical gap of \( \sim 0.13 \) mm for the measuring capacitor, this sample size allowed for the measurement of relative length changes, \( \left\{ \frac{\Delta L}{L} \right\} \), down to \( \sim 3 \times 10^{-8} \).
Measurements

These experiments were undertaken to determine the phase boundaries in the vicinity of the bicritical point of MnF₂. To determine points on the phase boundaries in the H-T plane (H|| [001]) two types of experiment were performed: a) the magnetostriction \( \frac{\Delta L}{L}(H) \) was measured by holding T fixed (by regulating the vapor pressure of a liquid nitrogen bath surrounding the capacitance cell) while H was slowly swept; or b) the thermal expansion \( \frac{\Delta L}{L}(T) \) was measured by holding H fixed while T was varied slowly (by allowing the vapor pressure of the bath to vary slowly). The fractional change in length of the MnF₂ crystal (along the [001] axis) and the swept variable (H or T) were simultaneously recorded digitally for later analysis by computer.

These magnetostriction and thermal expansion experiments were conducted in magnetic fields up to 140 kOe directed (nominally) along the c-axis. It is estimated that during the experiments, the magnetic field was applied within 2° of the c-axis.

A demagnetization correction amounting to about 0.4% of H was applied to the experimental data. To obtain this correction, a demagnetizing factor \( N=4\pi/3 \) was assumed. Such a value of N would hold for a spherical sample and it should be a fair approximation for the present near-cubic shape.

In all these experiments, T was measured using the calibrated Platinum resistance thermometer. In experiments of
type a, T was measured at H=0, and hence corrections for the magnetoresistance of the thermometer were not needed. In experiments of type b, however, T could only be measured at non-zero H, and corrections for the magnetoresistance were essential. As discussed in Chapter III, the maximum error in T that could have entered due to these magnetoresistance corrections was \pm 0.015 K at high fields.

Figs. (V.1) and (V.2) illustrate the determination of a point on the AF-P phase boundary by an experiment of type a. Fig. (V.1) shows a trace of \( \lambda(H,T) \) vs H at fixed \( T=66.73 \) K. The AF-P phase transition at \( H\approx 60 \) kOe is obvious, but its precise location is not so evident. Fig. (V.2) shows the result of the computer analysis of the data in Fig. (V.1) to extract \( (d\lambda/dH)_T \). There is a \( \lambda \)-like anomaly in \( (d\lambda/dH)_T \) at \( H=(61.1 \pm 0.7) \) kOe. Notice also in Fig. (V.2) that at low H (\( H\approx 40 \) kOe) the \( (d\lambda/dH)_T \) vs H curve is close to a straight line (i.e., \([\lambda(H)-\lambda(0)]aH^2\)). Such a behavior is predicted by the theory that will be presented in Chapter VI for the exchange magnetostriction.

Figs. (V.3) and (V.4) show the determination of another point (actually, the Néel temperature determination, at \( H=0 \)) on the AF-P phase boundary by an experiment of type b. Fig. (V.3) shows the sweep of \( \lambda \) vs T, and Fig. (V.4) the computer-extracted slope \( (d\lambda/dT)_H \). A \( \lambda \)-like anomaly is evident at the phase transition at \( T(=T_N)=(67.32 \pm 0.03)K \).
Fig. (V.1). A sweep of $\lambda(H, T)$ versus $H$ at $T=66.73$ across the AF-P phase boundary of MnF$_2$. 

MnF$_2$, $l \parallel c$

$T=66.73$ K
Fig. (V.2). The $H$-dependence of $\left(\frac{d\lambda}{dH}\right)_T$ extracted from the sweep in Fig. (V.1) by computer analysis.
\textbf{Fig. (V.3).} $\lambda(\mathbf{H}=0,T)$ versus $T$ in the vicinity of $T_N$ for MnF$_2$. 

MnF$_2$, $\mathbf{h} \parallel \mathbf{c}$

$\mathbf{H}=\mathbf{0}$
Fig. (V.4). The \(\lambda\)-like anomaly in \((d\ell/dT)_{H=0}\) used to locate the Néel point of MnF\(_2\).
The Phase Boundaries Near $T_b$

The phase boundaries of MnF$_2$ (in particular, the AF-P and SF-P boundaries) have been investigated previously by a variety of techniques. Those include NMR\(^{(5)}\) at low fields, ultrasonic attenuation,\(^{(6, 7)}\) and differential magnetization.\(^{(6, 8)}\)

A comparison of the measured boundaries of MnF$_2$ and the predictions of the bicritical theory was first presented by Fisher\(^{(9)}\) who performed a "rough analysis" of the data of Shapira and Foner\(^{(6)}\) to extract the parameters needed by the theory. More recent, and more accurate, data by King and Rohrer\(^{(8)}\) and by Shapira and Becerra\(^{(7)}\) have also been used to test the predictions of the theory.

The phase boundaries as measured in the present experiments in magnetic fields $H$ up to 140 kOe are shown in Figs. (V.5) and (V.6), in the $H$-$T$ and $H^2$-$T$ planes, respectively. The phase boundaries are in good agreement with the previous measurements\(^{(5-9)}\) of their positions. Examining these phase boundaries, especially as plotted in Fig. (V.6) (in the $H^2$-$T$ plane), we make the following observations: 1) the AF-P phase boundary, although fairly straight, exhibits a definite curvature as $T \to T_b$; and 2) the $H \to 0$ limiting slope of this line is estimated to be $\left(\frac{dT_c}{dH^2}\right)_{H=0} = -(1.53 \pm 0.08) \times 10^{-10} \text{kOe}^2$. This value is in good agreement with the previously reported experimental values. The MFA, on the other hand, predicts a value\(^{(6)}\) $\left(\frac{dT_c}{dH^2}\right)_{H=0} = -(1.0 \pm 0.3) \times 10^{-10} \text{K/Oe}^2$. Thus, the actual AF-P
Fig. (V.5). The phase boundaries near the Néel temperature of MnF$_2$ plotted in the H-T plane for H|| easy axis. Points were determined from anomalies in the magnetostriction (at constant T) and in the thermal expansion (at constant H).
Fig. (V.6). The phase boundaries near the Néel temperature of MnF$_2$, plotted in the $H^2$-$T$ plane for $H \parallel$ easy axis.
boundary curves towards lower T with increasing H faster than the MFA predicts; and 3) the SF-P phase boundary is almost vertical in the $H^2$-T plane, showing a slight outward curvature (i.e., $T_C$ increases slightly as H is increased). This behavior is in marked conflict with the MFA prediction that the SF-P phase boundary is approximately a straight line with slope

$$\left(\frac{dT_C}{dH^2}\right)_{H=0} = \frac{1}{3}\left(\frac{dT_C}{dH^2}\right)_{H=0}. $$

Since the MFA is inadequate to explain several features of the experimental phase boundaries, we are led to a comparison of the boundaries with the predictions of the modern bicritical theory. The method used to effect this comparison is the least-squares fitting technique described in Chapter IV in connection with the experiments on the bicritical point of $Cr_2O_3$.

The results of some least-squares fits performed using only the data points with $H>100$ kOe are summarized in Table (V.1). Also included are some results of other investigators.

The bicritical theory, and in particular the definitions of the parameters, is presented in detail in Chapter II. That discussion gives the shapes of the AF-P and SF-P phase boundaries near $T_b$ in terms of the seven parameters $T_b$, $H_b$, $p$, $q$, $Q$, $\omega_{||}$, and $\phi$. In terms of the reduced variables $g=H^2-H_b^2$ and $t=(T-T_b)/T_b$, the AF-P boundary is given by

$$g_{||}-pt_{||} = -\omega_{||}(t_{||}+qg_{||})^\phi \tag{V.1}$$
TABLE (V.1)

THE BICRITICAL POINT OF MnF
(The parameters are defined on pages 45 - 46)

a) Parameters taken from experiment.

\[ q_1 = \frac{1}{T_b} \left[ \frac{d T_c}{d H^2} \right]_{H=0} = (2.36 \pm 0.08) \times 10^{-12} \text{ Oe}^{-2} \]

\[ p = T_b \left[ \frac{d H_{SF}^2}{d T} \right]_{T=T_b} = (1.3 \pm 0.3) \times 10^{10} \text{ Oe}^2 \]

\((T_{b0}, H_{b0}) = (64.84 \text{ K}, 119.3 \pm 0.8 \text{ kOe})\)

b) Parameters obtained from least-squares fitting to experimental data with \( n = 3 \) assumed. The types of fits are defined on pages 86 - 87. (Parameters in brackets are chosen by the fitting procedure.)

<table>
<thead>
<tr>
<th>Source</th>
<th>Present Experiments</th>
<th>Fisher(^{(9)})</th>
<th>Shapira &amp; Becerra (^{(7)})</th>
<th>King &amp; Rohrer(^{(8)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>type of fit</td>
<td>1 2</td>
<td>1</td>
<td>1 3</td>
<td>3</td>
</tr>
<tr>
<td>Q</td>
<td>2.51 2.51</td>
<td>2.51</td>
<td>2.51 2.51</td>
<td>2.5</td>
</tr>
<tr>
<td>( \phi )</td>
<td>1.25 1.25</td>
<td>1.25</td>
<td>1.25 (1.2-1.3)</td>
<td>(1.22)</td>
</tr>
<tr>
<td>( T_N (K) )</td>
<td>(64.806) (64.864)</td>
<td>(64.89)</td>
<td>(64.73-64.75)</td>
<td>64.793</td>
</tr>
<tr>
<td>( q (10^{-12} \text{ Oe}^{-2}) )</td>
<td>(0.81) 1.31</td>
<td>(0.76)</td>
<td>(0.69-0.84)(0.68-0.83)</td>
<td>(0.65)</td>
</tr>
</tbody>
</table>
TABLE (V.1): Continued

b): Continued

<table>
<thead>
<tr>
<th>Source</th>
<th>Present Experiments</th>
<th>Fisher(9)</th>
<th>Shapira &amp; Becerra(7)</th>
<th>King &amp; Rohrer(8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{\parallel}(10^{12}\text{Oe}^2)$</td>
<td>(1.59) (2.28)</td>
<td>(1.46)</td>
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<td>-</td>
</tr>
<tr>
<td>rms dev. (K)</td>
<td>(0.015) (0.069)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

c) Parameters obtained from least-squares fitting to experimental data with $n=2$ assumed.

<table>
<thead>
<tr>
<th>Source</th>
<th>Present Experiments</th>
<th>Shapira &amp; Becerra(7)</th>
<th>King &amp; Rohrer(8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>type of fit</td>
<td>1 2</td>
<td>1 3</td>
<td>-</td>
</tr>
<tr>
<td>$Q$</td>
<td>1.00 1.00</td>
<td>1.00 1.00</td>
<td>(1.5)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>1.18 1.18</td>
<td>1.18 (1.2)</td>
<td>(1.28)</td>
</tr>
<tr>
<td>$T_N$(K)</td>
<td>(64.815) (64.808)</td>
<td>(64.73-64.75)</td>
<td>64.793</td>
</tr>
<tr>
<td>$q(10^{-12}\text{Oe}^{-2})$</td>
<td>(1.39) 1.57</td>
<td>(1.48-1.54) (1.5)</td>
<td>(1.22)</td>
</tr>
<tr>
<td>$\omega_{\parallel}(10^{12}\text{Oe}^2)$</td>
<td>(1.64) (1.56)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>rms dev. (K)</td>
<td>(0.015) (0.030)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
and the SF-P boundary is given by

\[ g_{\perp} - pt_{\perp} = Qw_{\perp}(t_{\perp} + q_{\perp})^\phi . \]  

The bicritical theory provides estimates for the parameters \( \phi(n), Q(n), \) and \( q(n) = \frac{n+2}{3n} q_1. \) Here, \( q_1 = -\frac{1}{T_b} \left( \frac{dT_C^{(1)}}{dH^2} \right)_{H=0} \) is experimentally measured and \( n \) labels the symmetry: \( n=3 \) for a cylindrically symmetric material and \( n=2 \) for an orthorhombic material. Other experimental quantities are \( p = T_b \left( \frac{dH_{SF}^2}{dT} \right)_{T=0} \) and \( (H_{b0}, T_{b0}) \) which are used to parameterize the AF-SF phase boundary (or its extension) upon which the bicritical point is assumed to lie.

The definitions of the types of least-squares fits used to analyze the experimental boundaries are given in Chapter IV, pages 86 - 87. Each fit type varies two or three of the parameters, taking the other parameters from theory or experiment: fit type 1 allows \( q, T_b, \) and \( \omega_{\parallel} \) to vary; fit type 2 allows \( T_b \) and \( \omega_{\parallel} \) to vary; and fit type 3 allows \( q, \omega_{\parallel}, \) and \( \phi \) to vary.

Table (V.1a) lists the experimentally measured parameters. Table (V.1b) and (V.1c) give the results of fits performed using the assumptions of \( n=3 \) and \( n=2, \) respectively.

Examining only the results of the present experiments, we make the following observations: 1) The type 1 fits (which allows \( T_b, q, \) and \( \omega_{\parallel} \) to vary, all other parameters held fixed) produce about the same rms errors for both the \( n=3 \) and \( n=2 \)
models for the anisotropy. This error is essentially the scatter in the experimental data; 2) the value of q generated by the type 1 fit agrees better with the theoretically estimated q for the case of n=2 than for n=3; and 3) the type 2 fit for the n=2 model results in a much smaller rms deviation than for the n=3 model.

In Fig. (V.7) are plotted the phase boundaries in the H^2-T plane in the vicinity of the bicritical point as predicted using the parameters obtained from these alternative fitting procedures. Shown are: the data points used to do the fits; the type 1, n=2 fit (in essence, the best fit. The type 1 fit for n=3 which produced about the same rms error, would lie very close to this line); and the type 2 fits for n=2 and n=3. The unsuitability of the type 2, n=3 fit as a description of the data is evident. This means that if all the theoretically predicted parameters are used, the assumption of cylindrical symmetry (n=3) leads to a poor fit.

These observations suggest that the model of n=2 (orthorhombic anisotropy) seems to provide a better description of the experimental data than the model of n=3 (uniaxial anisotropy). This would imply that there is a small anisotropy in the (001) plane in MnF₂ which is sufficient to destroy the approximation of MnF₂ as having a pure uniaxial anisotropy.

Alternatively, we may retain the n=3 model if we modify the theoretical estimate for q, namely Eq. (II.31c),
Fig. (V.7). The phase boundaries of MnF$_2$ near $T_b$ according to the bicritical theory with parameters chosen by least-squares fits. The solid curve represents a type 1 fit for $n=2$. The broken curves show type 2 fits for $n=2$ and $n=3$. 
Notice that for both the \( n=2 \) and \( n=3 \) models, the type 1 fit (which allows \( q \), among other parameters, to vary) provides a good agreement between the experimental points and the fitted curves. Thus, if the relation in Eq. (V.3) between \( q \) and 
\[
\left( \frac{dT_C''}{dH^2} \right)_{H=0}
\]
is put aside, the model of \( n=3 \) can provide just as good a description of the phase boundaries as the model of \( n=2 \).

The results of the least-squares fits on the present experimental data may also be compared with the findings of other investigators, some of whose results are listed in Table (V.1). The parameter \( q \) as determined in the present experiments is in reasonable agreement with those determined in other experiments, for fits performed with the same value of \( n \). The other experiments also seem to indicate a preference for a \( n=2 \) rather than a \( n=3 \) model, or that the theoretical estimate of \( q \) in terms of \( (dT_C''/dH^2)_0 \) is inadequate for \( \text{MnF}_2 \).

Conclusions

The AF-P and SF-P phase boundaries of \( \text{MnF}_2 \) have been determined in magnetic fields up to 140 kOe by measurements of the \( \lambda \)-anomalies in the thermal expansion coefficient, \( (\partial \lambda / \partial T)_H \), and in \( (\partial \lambda / \partial H)_T \). The data were compared to the predictions of the MFA and to the bicritical theory developed by Fisher, Nelson, and Kosterlitz. From these comparisons, we conclude
that the MFA is inadequate to explain the shape of the boundaries. The bicritical theory, on the other hand, provides a good qualitative description of the phase boundaries. Moreover, quantitative agreement with the theory may be obtained if the parameters of the theory are suitably chosen. The method of least-squares fits was used to choose the parameters. By comparing the results of various fitting procedures, it was found that the results suggested that MnF$_2$ may have sufficient anisotropy within the (001) plane to invalidate the modeling of the crystal as a pure uniaxial material, at least for the purposes of the bicritical theory.

The phase boundaries found in the present experiments are in reasonable agreement with the previous experimental determinations. Further, the parameters for the bicritical theory extracted from the present data (using a least-squares fitting technique) are in reasonable agreement with other published results.
REFERENCES

CHAPTER VI

MAGNETOSTRICTION

In any measurement of magnetostriction two directions with respect to the crystalline axes are selected: the direction \( \hat{z} \) along which the sample's length \( \ell \) is being measured, and the direction of the magnetic field \( \hat{H} \). With these specified, the linear magnetostriction (at a given temperature) is defined to be

\[
\frac{\Delta \ell}{\ell} = \frac{\ell(H,T) - \ell(H=0,T)}{\ell(H=0,T)} \tag{VI.1}
\]

The volume magnetostriction can be defined in a similar manner as

\[
\frac{\Delta V}{V} = \frac{V(H,T) - V(H=0,T)}{V(H=0,T)} \tag{VI.2}
\]

For a cubic material, the linear magnetostriction can be divided into three parts:\(^{(1)}\):

\[
\frac{\Delta \ell}{\ell} = \lambda_{\text{isot}} + \lambda_{\text{anisotr}} + \lambda_N \tag{VI.3}
\]

The last term, \( \lambda_N \), is the magnetostriction due to the change in the magnetostatic energy, and is known as the form effect. This term is the only one which depends on the shape of the
sample. The intrinsic, material-determined magnetostriction is represented by the other two terms. \( \lambda_{\text{isot}} \) is the isotropic part of the magnetostriction. It is chosen to be independent of the directions of \( \vec{\mathbf{x}} \) and \( \vec{\mathbf{H}} \) and corresponds to a uniform volume dilation/expansion. Physically, \( \lambda_{\text{isot}} \) is mainly due to the strain dependence (i.e., volume dependence) of the isotropic exchange energy. The third term, \( \lambda_{\text{anisotr}} \), represents the dependence of the magnetostriction on the directions of \( \vec{\mathbf{x}} \) and \( \vec{\mathbf{H}} \). It arises mainly from the strain dependence of the anisotropy energy.

It was argued in the Introduction that the magnetostriction due to the strain dependence of the exchange energy was of major importance in interpreting the experimental results reported in this thesis (except for the data near the spin-flop transition of Cr\(_2\)O\(_3\)). To calculate the exchange magnetostriction, we thus adopt a model in which the only magnetic interactions of a magnetic ion are: 1) isotropic Heisenberg interactions with other magnetic ions; and 2) a Zeeman interaction with the magnetic field. For the materials studied here, it is usually sufficient to consider only the nearest and next-nearest neighbor exchange to provide a reasonable description of the magnetostriction. The physical cause for the isotropic magnetostriction is expected to be the dependence of the exchange constants on the volume, and the model will assume that this is the only magnetoelastic coupling which need be considered.
A generalized calculation of the magnetostriction of magnetic materials has been given by Callen and Callen.\textsuperscript{(2)} Starting with a microscopic Hamiltonian, they calculate the free energy and minimize it with respect to the strains which are allowed by the symmetry. Single spin and two spin magnetoelastic couplings are considered (arising, for example, from the strain dependence of the single-ion anisotropy energy or the isotropic exchange energy, respectively) and all symmetry-allowed couplings are considered. For our assumed magnetoelastic coupling (a volume dependent isotropic exchange) their procedure predicts that the magnetostriction is a uniform volume dilation/expansion if the crystal symmetry is cubic (as in EuS). In lower symmetry materials, there will also be anisotropic terms depending on the angle between $\hat{H}$ and the high symmetry axis (hexagonal, tetragonal, or trigonal).

In the next sections, two approaches for the calculation of the volume magnetostriction will be presented. The first is a simplified derivation along the lines of the Callen and Callen treatment. The second is based on a thermodynamic argument and on certain statistical-mechanical properties of our model. The equivalence of the two approaches will then be demonstrated and numerical predictions will be obtained for comparison with the experiments on EuS. The major emphasis of the discussion will be on the calculation of the magnetostriction in a cubic ferromagnet such as EuS. Where
appropriate, mention will be made of the modifications needed in materials with different symmetry properties.

Volume Magnetostriction and the Two-Spin Correlation Function

The model Hamiltonian that we adopt is

\[ H = -2 \sum_{ij} J_{ij} \hat{S}_i \cdot \hat{S}_j - g_i \mu_B \hat{H} \cdot \hat{S}_i \quad (VI.4) \]

where the exchange constants \( J_{ij} \) are taken to be volume dependent,

\[ J_{ij} = J_{ij}^{(0)} + \frac{\partial J_{ij}}{\partial V} \partial V \quad (VI.5) \]

The volume change \( \partial V \) is measured from a (fictitious) state in which the magnetoelastic coupling is absent. This state is obtained by setting \( J_{ij} = J_{ij}^{(0)} = \text{constant} \) and calculating the properties of the system. The magnetoelastic coupling is then treated as a perturbation. To first order, the free energy is given by

\[ \phi = \phi_{\text{unpert}} + \Delta H_e + \langle H_{\text{me}} \rangle \quad (VI.6) \]

Here, \( \phi_{\text{unpert}} \) is the free energy of the unperturbed state, \( \Delta H_e \) is the change in the elastic energy as the crystal distorts. If the only distortion is a volume change,

\[ \Delta H_e = \frac{1}{2} \left( \frac{\delta V}{V(0)\kappa} \right)^2 \quad (VI.7) \]
where $\kappa$ is the isothermal compressibility. $<H_{me}>$ is the average of the magnetoelastic coupling

$$H_{me} = -2\delta V \sum_{<ij>} \frac{\partial J_{ij}}{\partial V} \hat{S}_i \cdot \hat{S}_j$$

(VI.8)

the average being carried out in the unperturbed configuration. Thus,

$$<H_{me}> = -2\delta V \sum_{<ij>} \frac{\partial J_{ij}}{\partial V} \langle \hat{S}_i \cdot \hat{S}_j \rangle$$

(VI.9)

$$= -2\delta V \sum_{<ij>} \frac{\partial J_{ij}}{\partial V} S^2 \eta_{ij}$$

where $\eta_{ij} = \langle \hat{S}_i \cdot \hat{S}_j \rangle / S^2$ is the two-spin correlation function between the pair of spins $i$ and $j$, evaluated in the absence of magnetoelastic coupling. Substituting Eq. (VI.9) into Eq. (VI.6) and minimizing with respect to the volume strain $\delta V$, we obtain

$$\delta V = 2V \kappa S^2 \left( \sum_{<ij>} \frac{\partial J_{ij}}{\partial V} \eta_{ij} \right)$$

(VI.10)

Eq. (VI.10) relates the distortion induced by a magnetoelastic coupling to the properties of the system in the absence of the coupling. The assumption of cubic symmetry comes in mainly in Eq. (VI.7). In a material with lower symmetry, the volume strain $\delta V$ is coupled to other
(anisotropic) strains in the elastic energy. As a result, even if the only magnetoelastic coupling is that given by Eq. (VI.5), there will be anisotropic strains due to this coupling through the elastic energy. The general case is dealt with in detail by Callen and Callen(2).

Specializing to the case of two exchange constants $J_1$ and $J_2$ between $z_1$ and $z_2$ pairs of nearest and next-nearest neighbor spins, respectively, Eq. (VI.10) may be written as

$$\frac{\delta V}{V} = 2 S^2 \left\{ \frac{N z_1}{2} \frac{\partial J_1}{\partial V} \eta_1 + \frac{N z_2}{2} \frac{\partial J_2}{\partial V} \eta_2 \right\} = \nu_1 \eta_1 + \nu_2 \eta_2 , \quad (VI.11)$$

where $N$ is the number of spins and the coupling constant $\nu_n$ is

$$\nu_n = S^2 \left( \frac{N}{V(O)} \right) z_n \left( \kappa V(O) \frac{\partial J_n}{\partial V} \right) = -S^2 \frac{N}{V(O)} z_n \left( \frac{\partial J_n}{\partial \theta} \right)_T \quad (VI.12)$$

$\eta_1$ and $\eta_2$ are the average reduced two-spin correlation functions between nearest and next-nearest neighbors respectively.

The volume change as given by Eq. (VI.11) is relative to a state in which there is no magnetoelastic coupling. The volume change induced by a magnetic field (i.e., the volume magnetostriction) is

$$\frac{\Delta V}{V} = \frac{V(H)-V(O)}{V(O)} = \sum_{n=1,2} \nu_n \left[ \eta_n(H)-\eta_n(O) \right] . \quad (VI.13)$$

This will lead, assuming only a uniform volume dilation/ expansion, to a linear magnetostriction given by
\[
\frac{\Delta \lambda}{\lambda} = \frac{1}{3} \frac{\Delta V}{V} = \frac{1}{3} \sum_n \eta_n \left[ \eta_n(H) - \eta_n(0) \right] .
\] (VI.14)

Eq. (VI.11) may also be used to calculate the magnetic contribution to the linear thermal expansion coefficient. The magnetic contribution is just

\[
\alpha_m = \frac{1}{3} \sum_n \eta_n \frac{\partial \eta_n}{\partial T} .
\] (VI.15)

When a ferromagnet is cooled from \( T=\infty \) to \( T=0 \) in zero magnetic field, the parameters \( \eta_n \) in Eqs. (VI.11) or (VI.14) change from \( \eta_n(T=\infty)=0 \) to \( \eta_n(T=0)=1 \) so that the fractional change in volume caused by the magnetic interactions in this cooling process is equal to \( \Sigma \eta_n \). This provides one method of measuring the coupling parameters involved.

In principle, the parameters \( \eta_n \) are temperature dependent because the number of ions per unit volume, \( N/V \), and \( (\partial J/\partial P)_T = -V \kappa (\partial J/\partial V)_T \) depend on \( T \). In practice, however, the \( T \) variation of \( \eta_n \) is small. In EuO, where only \( \eta_1 \) need be considered, \( \eta_1 \) was estimated to change by \( \sim 2\% \) as \( T \) changed from 0 to 245 K. (3)

Relation to the Susceptibility

An alternative to Eq. (VI.13) for low \( H \) may be derived by considering the free energy \( \phi(T,P,H) \) of a sample, and its differential

\[
d\phi = -\Omega dT + VdP - IdH .
\] (VI.16)
This gives a Maxwell relation

\[ \left( \frac{\partial V}{\partial H} \right)_{T,P} = -\left( \frac{\partial I}{\partial P} \right)_{T,H} \quad \text{(VI.17)} \]

For a sufficiently low \( H \) that the susceptibility \( \chi = I/H \) may be taken to be independent of \( H \) (and equal to its zero field value \( \chi_0 \)), Eq. (VI.17) may be integrated to obtain

\[ \frac{\Delta V}{V} = -\frac{1}{2} \frac{H^2}{V} \left( \frac{\partial \chi}{\partial P} \right)_T \quad \text{(VI.18)} \]

Notice that for a ferromagnet, the assumption of constant susceptibility excludes consideration of the ordered phase (i.e., \( T > T_C \) must hold) while for an antiferromagnet, a region in which the low field susceptibility is almost independent of \( H \) can be found at any temperature.

The \( P \) dependence of \( \chi_0 \) occurs because the exchange constants \( J_n \) are volume (and hence \( P \)) dependent, so that Eq. (VI.18) becomes

\[ \frac{\Delta V}{V} = \frac{H^2}{2V} \sum_n \left( \frac{\partial \chi}{\partial J_n} \right)_T \left( \frac{\partial J}{\partial P} \right)_T \quad \text{(VI.19)} \]

In terms of the reduced magnetization \( \sigma = I/(Ng\mu_B S) = \chi_0 H/\mu_B S \) and using the definition of \( v_n \) (Eq. (VI.12)), this becomes

\[ \frac{\Delta V}{V} = \sum_n \frac{Ng^2 \mu_B^2}{8z_n^*} \frac{1}{\chi_0^2} \left( \frac{\partial \chi}{\partial J_n} \right)_T \sigma^2 = \sum_n v_n A_n \sigma^2 \quad \text{(VI.20)} \]
where

$$A_n(T) = \frac{Ng^2\mu_B^2}{2z_n} \frac{1}{\chi_0} \left( \frac{\partial \chi_0}{\partial J_n} \right)_{T, J_n \neq n} \tag{VI.21}$$

Comparing Eq. (VI.20) to the previous expression (Eq. (VI.13)) we expect that for low $H$

$$\Delta \eta_n(H,T) = \eta_n(H,T) - \eta_n(0,T) = A_n(T) \sigma^2(H,T) \ , \tag{VI.22}$$

since the coupling parameters $\gamma_n$ are arbitrary as far as these calculations are concerned. The next section demonstrates that, in fact, this relation follows directly from the statistical mechanics of the model.

Eq. (VI.22) may be generalized to arbitrary field $H$ by defining a function $A_n(H,T)$ such that

$$A_n(H,T) = \eta_n(H,T) - \eta_n(0,T) \left/ \sigma^2(H,T) \right. \ . \tag{VI.23}$$

In the limit of low $H$, $A_n(H,T) = A_n(T)$ as defined in Eq. (VI.21), so that the definition of $A_n(H,T)$ and $A_n(T)$ are consistent.

In the opposite limit, as $H \to \infty$, both $\sigma(H=\infty,T)$ and $\eta_n(H=\infty,T)$ become equal to 1 so that

$$A_n(\infty,T) = 1 - \eta_n(0,T) \ . \tag{VI.24}$$

Evaluating $A_n(H,T)$ is extremely simple in the Mean Field Approximation. The MFA treats the spins as statistically
independent, and as a result, \( \eta_n(H,T) = \sigma_i(H,T) \sigma_j(H,T) \). Here, \( i \) and \( j \) are a pair of \( n \)th nearest neighbors. Above the ordering temperature (\( T_C \) or \( T_N \)), \( \eta_n(O,T) = 0 \) (only under the MFA) because \( \sigma_i(H=0,T) = 0 \). Further, in a ferromagnet where all the spins are equivalent (or in an antiferromagnet consisting of two equivalent sublattices), \( \sigma_i(H,T) = \sigma_j(H,T) = \sigma(H,T) \) above the ordering temperature, so that the MFA predicts

\[
A_n(H,T) = 1 \quad \text{(MFA, T > } T_C \text{ or } T_N) \quad (\text{VI.25})
\]

The departure of \( A_n(H,T) \) from unity (at \( T > T_C \) or \( T_N \)) provides a measure of the deviation from mean-field-like behavior.

Relation of \( \eta_n(H,T) \) to \( \sigma(H,T) \)

The relation between \( \eta_n(H,T) \) and \( \sigma(H,T) \) at low \( H \) which is contained in Eq. (VI. 22) (with \( A_n(T) \) defined in Eq. (VI.21)) may be derived without going through the calculation of the magnetostriction. It is contained in the statistical-mechanics of our model Hamiltonian.

For the Hamiltonian of Eq. (VI.4) and if we ignore the magnetoelastic coupling, the partition function \( Z \) is given by

\[
Z = \text{tr} e^{-H/kT} = \text{tr} \exp \left\{ 2 \sum_{i,j} \frac{J_{ij}}{kT} \hat{S}_i \cdot \hat{S}_j + \frac{g_i B H}{kT} \hat{S}_i \hat{S}_{iz} \right\}.
\]

\( H \) is assumed to lie along the \( z \)-direction. Now, above \( T_C \) or \( T_N \), all the individual spins have the same average spin \( \sigma_i = \langle \hat{S}_{iz} \rangle / S \). As a result, we can write
The zero-field susceptibility is thus

$$\chi_0 = \left[ \frac{\partial I}{\partial H} \right]_{H=0} = N g v_B \frac{\partial \langle S^z \rangle}{\partial H} = kT \frac{\partial^2}{\partial H^2} \ln Z.$$

On the other hand, when all nth-nearest neighbors are equivalent, we can write

$$\eta_n(H,T) = \frac{2}{N z_n} \langle \sum_{<ij>} \hat{S}_i \cdot \hat{S}_j / S^z \rangle = \frac{kT}{N z_n S^2} \frac{\partial^2}{\partial J_n^2} \ln Z.$$

Here, the sum $<ij>_n$ goes over all distinct nth-nearest-neighbor pairs of spins. Above $T_C$ or $T_N$, $\eta_n(H,T)$ is even in field, so that to lowest order in $H$, we may write

$$\eta_n(H,T) - \eta_n(0,T) = \frac{kT}{N z_n S^2} \frac{H^2}{2} \frac{\partial^2}{\partial H^2} \ln Z.$$

which is just Eq. (VI.22) with $A_n$ defined in Eq. (VI.21).
Single Exchange Constant Case

A simplification occurs for a model having only a single exchange constant. From the statistical mechanics of the model, the partition function \( Z \) depends on the variables \( x = \frac{J_1}{kT} \) and \( y = g \mu_B H / kT \) only, i.e., \( Z = \tilde{Z}(x, y) \). As a result, the zero-field susceptibility, from Eq. (VI.28), is then given by

\[
\chi_0 \equiv \left[ kT \left( \frac{\partial^2}{\partial x^2} \ln Z \right) \right]_{H=0} = \left[ kT \left( \frac{g \mu_B}{kT} \right)^2 \left( \frac{\partial^2}{\partial y^2} \ln \tilde{Z}(x, y) \right) \right]_{y=0} = \frac{\tilde{\chi}_0(x)}{T} .
\]

Thus, \( (\chi_0 T) \) is a function of \( x = \frac{J_1}{kT} \) only, and so

\[
\frac{\partial \chi_0}{\partial J_1} = \frac{1}{T} \frac{\partial (\chi_0 T)}{\partial J_1} = -\frac{1}{J_1} \frac{\partial (\chi_0 T)}{\partial T} . \tag{VI.33}
\]

As a result, Eq. (VI.21) may be rewritten as

\[
A_1(T) = -\frac{N g^2 \mu_B^2 k}{2Z_1 J_1} \frac{1}{\chi_0^2} \frac{\partial (\chi_0 T)}{\partial T} . \tag{VI.34}
\]

Because of its experimental accessibility, Eq. (VI.34) is much more attractive than its alternative, Eq. (VI.21). The quantity \( \left[ \frac{\partial \chi_0}{\partial J_n} \right]_T \) is not measurable, but \( \left[ \frac{\partial (\chi_0 T)}{\partial T} \right]_J \) is. It may be obtained in a straightforward manner is susceptibility data of sufficient detail are available. Such an analysis was performed in connection with experiments on the magnetostriction of the antiferromagnet MnF\(_2\)\(^{(4)}\). It proved to be very successful in predicting the magnetostriction, not only
for the paramagnetic phase (above $T_N$), but also for the antiferromagnetic, ordered phase (below $T_N$).

**High Temperature Series Calculations**

In the preceding sections, the magnetostriction of an isotropic Heisenberg ferro- or antiferromagnet has been related to certain of its thermodynamic properties—the zero-field susceptibility or the two-spin correlation functions. Both $\eta_n$ and $\chi_0$ should be determined from the Hamiltonian in Eq. (VI.4) in the absence of any magnetoelastic coupling. To proceed further, these properties must be calculated. In the present work, we have used High Temperature Series Expansions(5) to calculate these properties at $T>T_C,T_N$. There is an extensive literature on these series, since they provide estimates of quantities of interest in the study of critical phenomena. The results obtained from High-Temperature Series are generally considered to be very reliable.

The essence of the technique is to expand the partition function $Z$ or the free energy $\phi$ in a power series in $J_1/kT$. Physical properties of the model material, such as $\chi_0$, are then calculated, also in the form of a power series. For example, $\chi_0$ is expanded as

$$\chi_0(T) = \chi_{\text{Curie}} \sum_{m=0}^{\infty} a_m x^m.$$  \hspace{1cm} (VI.35)

$\chi_{\text{Curie}} = C/T$ is the Curie susceptibility, $C = Ng^2\mu_B^2S(S+1)/3k$ is the Curie constant, and $x = J_1/kT$ is the expansion variable. If a
model with only a single exchange constant, $J_1$, is considered, the coefficients $a_m$ of the power series are constants. If two exchanges constants $J_1$ and $J_2$ are included, the $a_m$ are functions of $\alpha = J_2 / J_1$.

In principle, the coefficients of any such series (e.g., the $a_m$) can be determined exactly once the model Hamiltonian, the lattice structure, and the spin $S$ are specified. In practice, only the first few (perhaps up to $m=10$) coefficients have been calculated due to the labor involved in calculating the higher-order coefficients. Table (VI.1) gives a partial list of the available series coefficients in cubic lattices.

**TABLE (VI.1)**

**HIGH TEMPERATURE SERIES EXPANSIONS FOR THE SUSCEPTIBILITY IN CUBIC HEISENBERG MAGNETS**

<table>
<thead>
<tr>
<th>Model</th>
<th>Number of Available Terms</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single exchange constant, general spin $S$</td>
<td>7</td>
<td>6,7</td>
</tr>
<tr>
<td>Single exchange constant, $S = \frac{1}{2}$</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>Single exchange constant, $S = \infty$</td>
<td>$S$(FCC), $9$(BCC,SC)</td>
<td>9</td>
</tr>
<tr>
<td>Single exchange constant, $S = \infty$, non-zero $H$</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Two exchange constants, general $S$</td>
<td>6</td>
<td>11</td>
</tr>
</tbody>
</table>
An extrapolation procedure may be used to estimate coefficients which have not been calculated directly. The extrapolation is based on certain regularities in the values of the coefficients. When the ratios $a_m/a_{m-1}$ of successive coefficients are plotted against $1/m$, they seem to follow a fairly smooth curve towards a definite $1/m\to 0$ intercept. Such a behavior would be expected by the scaling theories for quantities near $T_C$ in a ferromagnet, for example. Near $T_C$, but for $T>T_C$, the susceptibility is expected to diverge as

$$\chi_0 \sim (T-T_C)^{-\gamma} \sim (x_c-x)^{-\gamma}$$

(VI.36)

where $x_c=J_1/kT_C$ and $\gamma$ is the critical exponent for the zero-field susceptibility. To obtain such a divergence from the series expansion, we must have(12)

$$\frac{a_m}{a_{m-1}} \sim \frac{1}{x_c} \left[ 1 + \frac{(\gamma-1)}{m} \right] \text{ as } m\to \infty$$

(VI.37)

By plotting the known ratios $a_m/a_{m-1}$ versus $1/m$ and extrapolating to $1/m\to 0$, estimates for $x_c$ and $\gamma$ relevant to the model considered may be obtained. The extrapolation procedure based on Eq. (VI.37) is known as the "ratio method" (or "slope method") for determining the critical properties. It results from the application of a simple ratio test to determine the circle of convergence of the power series in Eq. (VI.35). The singularity at $x=x_c$ (i.e., at the phase transition) limits this
circle of convergence. More sophisticated methods\(^{(12)}\) of series analysis may be used to provide better estimates of \(x_c\) and \(\gamma\). Such estimates are in themselves useful in the theory of critical phenomena. More importantly (as far as the present work is concerned), once values of \(x_c\) and \(\gamma\) are obtained (by whatever means), estimates of the higher order coefficients may be made and the series may then be evaluated fairly accurately even very close to the transition temperature.

Eq. (VI.37) suggests that a recursion relation of the form

\[
a_m = R(m)a_{m-1}
\]

(VI.38)

with

\[
R(m) = \frac{1}{x_c} + \frac{\gamma - 1}{x_c} \frac{1}{m} + D \frac{1}{m^\gamma}
\]

(VI.39)

be used to estimate unknown coefficients. In this estimate, \(D\) is chosen to match the ratio of the last two exactly known coefficients.

By following this extrapolation procedure, we have obtained numerical estimates of the functions relevant to our magnetostriction theory. Most of the calculations started with an available series expansion of \(X_0\), in the form of Eq. (VI.35). The exact values of the low-order coefficients were taken from the references quoted in connection with Table (VI.1). Estimates for \(x_c\) and \(\gamma\) were taken from those same references and/or
obtained by re-analyzing the known coefficients using the ratio method and the Neville table method of series analysis\(^{(12)}\). With these values specified, the extrapolation procedure gave an estimate for all the coefficients \(a_m\). By summing numerically the infinite series in Eq. (VI.35), the function \(\chi_0(T)\) was estimated. \(A_n(H=0,T)\) was obtained by using Eq. (VI.21) to relate \(A_n\) to the derivatives of \(\chi_0\) and to \(\chi_0\) itself.

The numerical calculations were performed for most of the series listed in Table (VI.1). All the series are based on the isotropic Heisenberg Hamiltonian (as in Eq. (VI.4), with the \(J_{ij}\) held fixed). Different series are generated depending on the choice of: 1) the lattice symmetry (e.g., FCC, BCC, or SC); 2) the spin quantum number, \(S\); and 3) the number of distinct exchange constants (e.g., nearest-neighbor exchange only, or nearest plus next-nearest neighbor exchange). The results of the numerical evaluations of \(A_n(H=0,T)\) are presented in Figs. (VI.1-5).

Figs. (VI.1) and (VI.2) show curves of \(A_1(0,T)\) calculated\(^{(13)}\) for a model with a single exchange constant. The curves are truncated at some temperature above \(T_C\) (or \(T_N\)) when the calculated \(A_1\) values become "unreliable"—i.e., alternative extrapolation procedures (such as varying \(x_c\) or \(y\) within their error bars, or fixing \(D=0\), etc.) start giving answers which differ by more than \(\pm 2\%\). This truncation criterion is used in drawing all the figures in this chapter.
Fig. (VI.1). The temperature dependence of $A_1(H=0,T)$ for BCC Heisenberg ferromagnets and antiferromagnets with only an isotropic nearest-neighbor exchange interaction. $S$ is the spin quantum number.
Fig. (VI.2). The $T$-dependence of $A_1(H=0,T)$ for FCC Heisenberg ferromagnets with only an isotropic nearest-neighbor exchange interaction.
Fig. (VI.3). The $T$-dependence of $A_1(H=0,T)$ for a FCC Heisenberg ferromagnet with two exchange constants, $J_1$ and $J_2$. Curves are shown for several choices of the ratio $\alpha = J_1/J_2$. 
Fig. (VI.4). The $T$-dependence of $A_1(H=0,T)$ and $A_2(H=0,T)$ for an FCC Heisenberg ferromagnet with a nearest-neighbor exchange constant only.
Fig. (VI.5). The $T$-dependence of $A_1(H,T)$ for a classical ($S\rightarrow\infty$) FCC ferromagnet with nearest-neighbor interactions only. The upper curve is for the limit $H\rightarrow\infty$ and the lower curve is for $H=0$. 
Fig. (VI.1) contrasts the BCC ferromagnet and antiferromagnet for a few different spin quantum numbers. In the MFA, \( A_1(H,T) = 1 \) for any \( H \) and any \( T > T_C \) or \( T_N \). In these more exact calculations, the curves deviate from this MFA behavior as \( T \) is decreased towards the ordering temperature from above. In a ferromagnet, \( A_1(0,T) \) decreases towards zero as \( T \) is brought near \( T_C \) from above. In contrast, for an antiferromagnet, \( A_1(0,T) \) increases as \( T \to T_N \) from above. Such behavior is as expected. In a ferromagnet, if we use the definition of \( A_1(0,T) \) in Eq. (VI.34) and the assumed divergences of \( \chi_0 \) given in Eq. (VI.36), then one would expect that near \( T_C \),

\[
A_1 \propto (T-T_C)^{\gamma-1}.
\]

For a three-dimensional Heisenberg ferromagnet, \( \gamma \approx 1.4(8, 9) \) so that \( A_1 \to 0 \) as \( T \to T_C \) from above. On the other hand, in an antiferromagnet, the derivative of the susceptibility with respect to \( T \) exhibits a \( \lambda \)-like peak at \( T_N \). Thus, \( A_1 \) is very large (possibly infinite) at \( T_N \).

Fig. (VI.3) shows the effects introduced when the second exchange constant \( J_2 = \alpha J_1 \) is included. The calculations are for an \( S=7/2 \) FCC ferromagnet. (EuS is such a material with \( \alpha \approx -0.45 \)). Plotted are the \( A_1(0,T) \) curves for several choices of \( \alpha \). A positive (ferromagnetic) \( J_2 \) tends to increase the value of \( A_1 \) for a given value of \( T/T_C \). A negative (antiferromagnetic) \( J_2 \) decreases the value of \( A_1 \).

Fig. (VI.4) compares \( A_1(0,T) \) with \( A_2(0,T) \). The calculations were performed for a model with only a single exchange constant (i.e., \( J_2 = 0 \)). As one might expect, the behavior of
A_2 is much closer to the MFA prediction—spins which are farther away from each other behave as if they were less correlated, more statistically independent, and hence more MFA-like.

We now turn to the calculation of A_1(H,T) for a non-zero H. Unfortunately, many of the series expansions which would be of use in such calculations have not been evaluated. Some series, however, are available.

As H→∞, Eq. (VI.24) gives the limiting value of A_n(H,T), namely,

$$A_n(∞,T) = 1 - \eta_n(0,T).$$

High temperature series expansions for η_n(0,T) are available for a model with a single exchange constant and for several values of S. We have summed such series to estimate A_1(∞,T). The results for S=∞ are shown in Fig. (VI.5), which shows A_1(∞,T) and A_1(0,T). As is evident in the figure, The A_1(∞,T) curve lies above the A_1(0,T) curve, but still remains below the value 1.

To calculate A_1(H,T) at intermediate values of H, we have made use of a "double expansion" of the free energy. In this expansion, the free energy φ(H,T) is expanded in a double power series in the variables (J_1/kT) and (gμ_BH/kT). Only the single exchange constant, J_1, is included in this expansion. \(Δ\eta_1(H,T)\) and \(σ(H,T)\) can then be obtained, also in the form of a double series expansion, and the definition of A_1, Eq. (VI.23), used to calculate A_1(H,T). The double series
was extrapolated in the \((J_1/kT)\) variable, just as above, but no method for the extrapolation in the \((g\mu_B H/kT)\) variable is valid. The results are thus restricted so sufficiently low values of \(H\) (roughly, for fields where \(\sigma \leq 0.1\)). Some of the results of these calculations will be presented in connection with the experiments on EuS (mainly in Figs. (VII.2) and (VII.3)). For now, we remark that for fields where \(\sigma < 0.1\), \(A_1(H,T)\) is a slowly varying function of \(H\), increasing slowly from \(A_1(0,T)\) as \(H\) is increased.

The Relation Between \(T_C\) and \(J_n\)

One result of the analysis of high-temperature series expansions is an estimate for the quantity

\[
x_c(\alpha) = \frac{J_1}{kT_C}
\]  

(VI.41)

Hence, \(T_C\) and the \(J_n\) are related by the theory and may not be specified completely independently. In general, the estimate of \(T_C\) obtained from Eq. (VI.41) using experimental values for \(J_1\) and \(\alpha\) does not agree exactly with the measured \(T_C\)\(^{(16)}\). The discrepancy is often attributed to the effect of dipole-dipole interactions.\(^{(17)}\)

For example, for EuS, theory estimates \(T_C=15.52\) K using the values of \(J_1\) and \(J_2\) given in Chapter VII. The measured value is \(T_C=16.49 \pm 0.04\) K.

This relation between \(T_C\) and the \(J_n\) comes into play when a comparison of experimental results with theory is to be
performed—the parameters needed by the theory ($J_1$ and $J_2$) are overspecified by experimental data for $J_1$, $J_2$, and $T_C$. In view of the importance of $T_C$ in its role of ordering temperature, the method used in this thesis to resolve this overspecification is to choose $J_1$ and $J_2$ so as to match the experimental $T_C$. The ratio $\alpha=J_1/J_2$ is taken to be equal to the ratio of the measured exchange constants.
REFERENCES

CHAPTER VII

THE MAGNETOSTRICTION OF EuS

Properties of EuS

EuS crystallizes in the rocksalt structure in which the magnetic Eu$^{++}$ ions form an FCC lattice with lattice constant 5.968 Å at 300 K. The magnetic properties are mainly due to the 4f electrons, with the ion being in the spherically symmetric $^{8}_{7/2}$ spin state and having a $g$ value 1.992 ±0.001 (1-3). EuS is a ferromagnet with a Curie temperature $T_C$ ≈ 16.5 K.

The dominant exchange interactions are a ferromagnetic exchange between an ion and its $z_1$=12 nearest neighbors, and an antiferromagnetic exchange with its $z_2$=6 next-nearest neighbors. From measurements of the specific heat at low temperatures (4, 5), the exchange constants are (6) $J_1/k=0.228 \pm 0.008$ K and $J_2/k=-0.102 \pm 0.005$ K.

Because of the spherically symmetric ground state of the Eu$^{++}$ ion and the cubic symmetry of the crystal, the anisotropy is expected to be small. EuS is found experimentally (7) to have the (cubic) anisotropy constants $K_1/M_S=19.6 \pm 1.0$ Oe and $K_2/M_S=4.6 \pm 0.3$ Oe, where $M_S$ is the saturation magnetization, $M_S \approx 1200$ erg/cm gauss at $T=0$. The easy directions of magnetization are the [001] and equivalent directions.
EuS belongs to the family of materials known as the Europium-Chalcogenides, the other members being EuO, EuSe, and EuTe. All these materials have the same crystal structure and exhibit magnetic ordering at low temperatures. All have a positive (ferromagnetic) \( J_1 \) which decreases in magnitude from the oxide to the telluride. \( J_2 \) is believed\(^8\) to be positive (ferromagnetic) in EuO and negative (antiferromagnetic) in the other compounds, increasing in magnitude from the sulfide to the telluride. In EuO and EuS, the nearest-neighbor exchange is dominant, and both materials are ferromagnets. In EuTe, on the other hand, the next-nearest-neighbor exchange dominates, and EuTe is an antiferromagnet. EuSe lies between these two extremes. It has \( z_1 |J_1| \approx z_2 |J_2| \), and as a result has a complicated phase diagram with a number of different types of magnetic order.

The magnetostriction of EuO has been measured\(^9, 10\) and agrees well with a single-exchange-constant Heisenberg model. The effects of the second (and further) exchange constants are expected to become much more important in the other chalcogenides, and in particular in EuS, which is the subject of this investigation.

**Sample and Sample Preparation**

The sample used in the present experiments was an insulating single crystal disk of diameter 6.2 mm and thickness 1.22 mm (obtained from Professor G. E. Everett, University of California in Riverside). The faces of the disk were (001)
faces, within 1° as checked with x-rays, and were lapped flat and parallel.

The Curie Temperature

To determine the Curie temperature, the thermal expansion at $H=0$ was measured near $T_C$. The experimental procedure was similar to that described for the determination of $T_N$ in Cr$_2$O$_3$ and MnF$_2$. The temperature of the sample was slowly varied by changing the vapor pressure of the liquid hydrogen bath in which the capacitance cell was immersed. The thermal expansion was then measured as a function of temperature (the temperature was measured with a calibrated germanium thermometer). The thermal expansion coefficient $\frac{1}{\xi} \frac{d\xi}{dT}$ at $H=0$ exhibited a $\lambda$-like peak at $T_C$. Fig. (VII.1) shows this peak obtained from a computer analysis of a sweep in temperature. From such sweeps, the Curie temperature was measured as $T_C=16.49 \pm 0.04$ K. The polarity of the $\lambda$-anomaly (i.e., a peak in $\frac{1}{\xi} \frac{d\xi}{dT}$) agrees with x-ray data on the lattice parameter.

Measurements

The isothermal longitudinal and transverse magnetostrictions were measured along the [001] direction ($\hat{\xi}||[001]$). The longitudinal magnetostriction was measured with $\hat{H}||\hat{\xi}$ (to within 2°) and the transverse magnetostriction was measured with $\hat{H}||\hat{\xi}$ ($\hat{H}||[010]$ to within 5°). Data were taken at temperatures $T>T_C$, between 16.8 K and 146 K, in magnetic fields up to 140 kOe. Detailed data for $T$ close to $T_C$ (16.8 K to 20 K)
Fig. (VII.1). The thermal expansion coefficient 
\[ \frac{1}{\xi} \left( \frac{d\xi}{dT} \right)_{H=0} \] near the Curie temperature of EuS.
were taken at low fields \((H \leq 3 \text{ kOe})\) by using a 500 A current supply (rather than the Laboratory's 22 kA dc generators) in conjunction with a Bitter-type solenoid magnet.

The magnetic moment of this same sample, with \(\vec{\mu} || [010]\), was measured by S. Foner and E. J. McNiff, Jr. at the same \(T\) and \(H\) values as the magnetostriction measurements. They used a "very low frequency vibrating sample magnetometer"(12) installed in Bitter-type solenoid magnets. Additional magnetization measurements at 4.2 K were performed in a superconducting magnet using a "vibrating sample magnetometer"(13), primarily to obtain the demagnetizing factors.

Because of the importance of the reduced magnetic moment \(\sigma(H,T)\) in the theoretical discussion of the magnetostriction, the measured magnetic moment was normalized to its saturation value (at low \(T\) and high \(H\)). The saturation magnetization was \(M_S = 203 \pm 5 \text{ emu/gm}\), corresponding to \((6.7 \pm 0.2)\mu_B\) per \(\text{Eu}^{++}\) ion.

**Demagnetization Correction**

Much of the magnetostriction data were taken at low \(H\) for \(T\) near \(T_C\). In such situations, the corrections for the demagnetizing field \((-\vec{M})\) were very important, i.e., the demagnetizing field could be an appreciable fraction of the applied external magnetic field \(H_{\text{ext}}\).

To analyze the magnetostriction data, it was assumed that the effective demagnetizing factors which entered into the magnetostriction measurements were equal to the ones which
entered into the magnetic moment measurements. The effective demagnetizing factors were obtained from the initial slope of the magnetic moment curve at 4.2 K,

$$N^{-1} = \frac{1}{V} \left( \frac{dI}{dH_{\text{ext}}} \right)_{H_{\text{ext}} = 0}$$  \hspace{1cm} (VII.1)

The values obtained were $N=1.98 \pm 0.10$ for $\hat{H}||[010]$, i.e., for $\hat{H}$ in the plane of the disk, and $N=7.99 \pm 0.2$ for $\hat{H}||[001]$, i.e., for $\hat{H}$ perpendicular to the plane of the disk.

To calculate $H_{\text{int}}$ from $H_{\text{ext}}$, the measured $\sigma(H_{\text{ext}}, T)$ was substituted into Eq. (III.5) using these values for $N$. As mentioned above, $\sigma(H_{\text{ext}}, T)$ was measured only for the configuration $\hat{H}||[010]$. Values for the other configuration were calculated using the two values for $N$.

It is clear that the procedure used to correct for the demagnetizing field was not rigorously correct. To estimate the errors that might have been generated, the effective demagnetizing factors were also obtained from magnetostriction (rather than magnetic moment) measurements at 4.2 K. As the sample was magnetized, the processes of domain growth and domain rotation were accompanied by a magnetostriction which became saturated at a field $H_{\text{ext}} \approx N M_S$. The saturation magnetization $M_S$ was known. In this way, the values $N=8.0 \pm 0.4$ for $\hat{H}||[001]$ and $N=1.6 \pm 0.2$ for $\hat{H}||[010]$ were obtained. (These values, and the previous ones, might be compared to those calculated\(^{(14)}\) for an oblate ellipsoid with the same ratio of
diameter to thickness as the disk used in these experiments. For a ratio of 5, \( N=9.42 \) for \( \mathbf{H} \) parallel to the short axis and \( N=1.57 \) for \( \mathbf{H} \) perpendicular to the short axis.

The effect of this \( \approx 25\% \) difference between the value of \( N \) (for \( \mathbf{H} || [010] \)) obtained by the two experimental methods was considered. The values for \( N \) entered into the data analysis in two ways: in the calculation of \( H_{\text{int}} \) from \( H_{\text{ext}} \) (for either configuration); and in the determination of \( \sigma(H_{\text{ext}}) \) for the configuration \( \mathbf{H} || [001] \) from \( \sigma(H_{\text{ext}}) \) data for \( \mathbf{H} || [010] \). At elevated temperatures (\( T>77 \) K), the effect of the uncertainty in \( N \) was negligible (no more than 0.2\% in \( H_{\text{int}} \) or \( \sigma \)). At lower temperatures (i.e., close to \( T_C \)), the uncertainty in the value of \( N \) could have had a much more significant effect. \( H_{\text{int}} \) would have been shifted by an amount \( \nabla(\Delta N)M_s \sigma \), where \( \Delta N=0.4 \) was the uncertainty in \( N \). In the worst case (at the lowest temperature) this would have amounted to a 15\% uncertainty in \( H_{\text{int}} \). More typically, the possible errors were 5-10\%. The uncertainties introduced into the determination of \( \sigma \) for \( \mathbf{H} || [001] \) were at worst 5\%, and typically 2-3\%.

The effect of these possible errors on the analysis of the magnetostriction data will not result in any major modifications of the results and conclusions of the present work. For example, as discussed in Chapter VI as well as later in this chapter, the ratio \( (\Delta V/V/\sigma^2)_{\sigma=0} \) and its \( T \) dependence are very important in characterizing the magnetostriction. In EuS, we will find that \( (\Delta V/V/\sigma^2)_{\sigma=0} \) changed by a factor of \( \approx 3 \) as the
temperature was lowered from $T \approx 80$ K down to $T/T_C = 1.02$. The (at most) 10% error in $\sigma^2$ will not qualitatively alter this behavior.

Experimental Results

Figs. (VII.2) and (VII.3) show some of the measured magnetostriction curves (for the longitudinal configuration) plotted against $H_{\text{int}}^2$. Fig. (VII.2) shows data at high temperatures ($T \approx 4T_C$) where the normalized susceptibility $\bar{\chi} = \sigma/H_{\text{int}}$ changed only slightly from its zero field value, even at fields up to 120 kOe. $\Delta \ell/\ell$ was then roughly proportional to $H_{\text{int}}^2$, for $H_{\text{int}}$ up to 120 K the deviation from exact proportionality being mainly due to the slight $H$ dependence of $\bar{\chi}$. This deviation became much more noticeable as $T$ decreased. The range of fields over which $\Delta \ell/\ell$ was roughly proportional to $H_{\text{int}}^2$ became smaller and smaller as $T$ approached $T_C$ owing to the much stronger $H$ dependence of $\bar{\chi}$. However, even at temperatures only a few degrees above $T_C$, it was possible to obtain data at sufficiently low fields so that the ratio $(\Delta \ell/\ell)/H_{\text{int}}^2$ did not vary appreciably. This is illustrated by the low-temperature ($T \leq 1.2 T_C$) data in Fig. (VII.3). Notice that in this figure, the maximum field is only $H_{\text{int}} \approx 1.5$ kOe (in contrast to $\approx 120$ kOe in Fig. (VII.2) for the high temperatures).

The dashed lines in Figs. (VII.2) and (VII.3) are tangents to the magnetostriction versus $H_{\text{int}}^2$ curves at $H_{\text{int}} = 0$, estimated from the experimental points. These estimates were obtained by fitting the data to equations of the form
Fig. (VII.2). The longitudinal magnetostriction of EuS versus $H_{int}^2$ at several temperatures well above $T_C$. The dashed straight lines are tangents to the experimental curves at $H_{int}=0$. The solid curves are the results of calculations using the approximation in Eq. (VII.5).
Fig. (VII.3). The longitudinal magnetostriction of EuS versus $H_{\text{int}}$ at several temperatures near $T_C$. The dashed lines are tangents to the experimental curves at $H_{\text{int}}=0$. The solid curves are calculated using the approximation in Eq. (VII.5).
\[ \frac{\Delta \ell}{\ell} = B H^2_{\text{int}} \]  

(VII.2)

and

\[ \frac{\Delta \ell}{\ell} = B H^2_{\text{int}} + B' H^4_{\text{int}} \]  

(VII.3)

By decreasing the range of points in the fit, the \( H=0 \) tangent \( B_0 \) was then estimated.

The maximum field in these figures has been restricted so that the deviations of the experimental points from the tangent line were not excessive. We have attributed these deviations mainly to the \( H \) dependence of \( \bar{\chi} \). Measurements of \( \sigma(H_{\text{int}}) \) and hence \( \bar{\chi}(H_{\text{int}}) \) were available so that an analysis of the experimental data with the effects of the actual \( H \) dependence of \( \bar{\chi} \) included could be performed. Such an analysis will be described later, but first we present a simple theoretical estimate of the deviations.

The basis of any attempt to include the \( H \) dependence of \( \bar{\chi} \) in the analysis of the \( \Delta \ell/\ell \) data is Eq. (IV.20) (or variants of it), namely,

\[ \frac{\Delta \ell}{\ell}(H) = \left[ \sum_n \frac{\nu_n A_n(H,T)}{3} \right] \sigma^2(H) = \left[ \sum_n \frac{\nu_n A_n(H,T)}{3} \right] \bar{\chi}(H) H^2 \]  

(VII.4)

Calculations based on double series (in \( J_1/kT \) and \( H/kT \)) for a model with a single exchange constant indicate that the \( H \) dependence of \( \bar{\chi} \) is in general much stronger than that of \( A_n \).
The deviations of the $\Delta l/l$ vs $H^2$ curve from the tangent line will then be due mainly to the non-constant $\bar{x}$. This also explains why the $(\Delta l/l)$ vs $\sigma^2$ plots are expected to be straighter than the $(\Delta l/l)$ vs $H_{\text{int}}^2$ plots.

To obtain an estimate for the $H$-dependence of $\Delta l/l$ we used a double series expansion (in $H/kT$ and $J_1/kT$) for the single-exchange-constant $S=\infty$ Heisenberg model (see Table (VI.1)). We have used this expansion to calculate $\frac{\Delta l}{l}(H)_{\text{model}}$ in terms of the single coupling constant $\nu_1$. (For this model, only the $n=1$ term in Eq. (VII.4) contributes.) EuS is not expected to behave exactly like such a model (especially as $J_2$ is ignored). Thus, major discrepancies occur in the prediction of the $T$ dependence of the initial slope, $B_0$. Nonetheless, we have used the model calculations to estimate the $H$-dependence of $\Delta l/l$ (at fixed $T$) by writing

$$\left[\frac{\Delta l(H)}{l}\right]_{\text{est.}} = \frac{B_0(\text{measured})}{B_0(\text{model})} \left[\frac{\Delta l(H)}{l}\right]_{\text{model}} \quad (\text{VII.5})$$

That is, we have forced the $H=0$ tangent of the estimating curve to coincide with the measured tangent. The model calculations then gave an estimate of the deviations from that line. The solid curves in Figs. (VII.2) and (VII.3) represent the results of such calculations. The experimental and estimated curves are similar. The deviations are probably due (at least in part) to the fact that $J_2$ was omitted.
To combine the measured $\sigma(H,T)$ in the analysis, a procedure suggested by Eq. (VII.4) was undertaken. When $\Delta l/l$ was plotted against $\sigma^2$, curves such as in Figs. (VII.4) and (VII.5) were obtained. In Fig. (VII.4), only the high-temperature ($T>4T_C$) data are plotted. In this temperature range, the parameters $A_n(H,T)$ are all expected to be approximately equal to unity, and hence nearly $T$ and $H$ independent. As a consequence, the data for all three temperatures should (and do) lie along the same straight line. This is not the case in Fig. (VII.5) because for this figure, the temperature is low enough that the $T$-dependence of the $A_n$ is evident.

Even when $T$ was very close to $T_C$ (e.g., the 16.96 K points in Fig. (VII.5)), the experimental points (at $T$ fixed and for low $H$) fell very nearly along a straight line. It was then possible to determine the initial slopes (as $\sigma \to 0$, which is equivalent to $H \to 0$) of the $\Delta l/l$ vs $\sigma^2$ curves much more reliably than the $\Delta l/l$ vs $H_{\text{int}}^2$ slopes. The initial slopes were determined using least-squares fits to equations of the form

$$\frac{\Delta l}{l} = \xi_1 \sigma^2,$$  \hspace{1cm} (VII.6)

$$\frac{\Delta l}{l} = \xi_1 \sigma^2 + \xi_2 \sigma^4.$$  \hspace{1cm} (VII.7)

Again, the number of points entering the fit was varied so that the $\sigma \to 0$ slope $\left[\frac{\Delta l}{l}/\sigma^2\right]_0$ could be determined. Because of the (relative) ease of extracting $\left[\frac{\Delta l}{l}/\sigma^2\right]_0$ from the experimental data and in view of the uncertainties in $H_{\text{int}}$ due to the
Fig. (VII.4). The longitudinal magnetostriction of EuS versus $\sigma^2$ at several temperatures well above $T_C$. 
Fig. (VII.5). The longitudinal magnetostriction of EuS versus $\sigma^2$ at several temperatures just above $T_C$. 
uncertainties in the demagnetizing factors, we have focused on the quantity \( \frac{\Delta l}{l} / \sigma^2 \) for comparison with theory.

The \( H=0 \) Slopes of \( \frac{\Delta l}{l} \) vs \( \sigma^2 \)

Fig. (VII.6) shows the \( H=0 \) slopes of the \( \frac{\Delta l}{l} \) vs \( \sigma^2 \) curves (i.e., the \( H=0 \) intercept of the quantity \( \left( \frac{\Delta l}{l} / \sigma^2 \right) \)) as measured in these experiments. Points are shown for the two configurations \( \vec{H} \parallel \vec{z} \) and \( \vec{H} \perp \vec{z} \). \( \left( \frac{\Delta l}{l} / \sigma^2 \right) \) has been plotted against the quantity \( \log(T-T_C) \). Such a plot emphasizes the region very close to \( T_C \). Three theoretical curves are also shown for reference. These curves are based on Eq. (VII.4) where the \( A_n \) have been calculated according to either the Mean Field Approximation or High Temperature Series Expansions (with two exchange constants, parameterized for EuS). The choice of the \( \nu_n \) is discussed extensively in the next section. For the present we remark that the quantity \( (\nu_1+\nu_2) \) can be obtained from other experiments but the ratio \( \nu_2/\nu_1 \) cannot be reliably determined. For the purposes of this plot, the ratio has been set (arbitrarily) equal to 1 or zero.

For either configuration, \( \vec{H} \parallel \vec{z} \) or \( \vec{H} \perp \vec{z} \), the qualitative features of the experimental curves are the same. At high \( T \) (e.g., the \( T\lessgtr 4T_C \) points), the value of \( \left( \frac{\Delta l}{l} / \sigma^2 \right)_0 \) remains relatively constant. However, as the temperature is lowered towards \( T_C \), the magnitude of \( \left( \frac{\Delta l}{l} / \sigma^2 \right)_0 \) decreases considerably.

The MFA predicts that \( A_n(H,T)=1 \) for all \( T>T_C \) and for all \( n \). Thus, except for the slight temperature dependence of
Fig. (VII.6). The $\sigma \to 0$ limit of the ratio of the magnetostriction, $(\Delta l/l)$, to the square of the reduced magnetization, $\sigma^2$. Data are shown for both the longitudinal ($\bar{H} \parallel \bar{l}$) and transverse ($\bar{H} \perp \bar{l}$) configurations. The curves are the results of theoretical calculations based on Eq. (VII.4). The parameters $A_\| (H=0,T)$ in that equation are calculated using the MFA or the method of high-temperature series expansions. The value $\nu_{\text{tot}} = \nu_1 + \nu_2 = -1.12 \times 10^{-3}$ is used for all the curves.
the \( v_n \), the MFA predicts that \( \left( \frac{\Delta \mathcal{L}}{\mathcal{L}} / \sigma^2 \right)_0 \) should be a constant for all the \( T > T_C \). When this prediction is compared to the experimental data, as in Fig. (VII.6), significant deviations are evident, especially for \( T \) near \( T_C \), and we must conclude that the MFA is inadequate to explain the experimental data. The high-temperature-series prediction is in much more reasonable agreement.

The experimental points in Fig. (VII.6) span a temperature range \( 1.02 \leq T / T_C \leq 0.9 \). Over this range, the normalized zero-field susceptibility \( \overline{\chi}_0 = (\sigma / H)_{H=0} \) changed by \( \sim 3 \) orders of magnitude (see Fig. (VII.8), which is discussed later). The quantity \( \left( \frac{\Delta \mathcal{L}}{\mathcal{L}} / \sigma^2 \right)_0 \) changed by almost 6 orders of magnitude. Yet, the quantity \( \left( \frac{\Delta \mathcal{L}}{\mathcal{L}} / \sigma^2 \right)_0 \) changed by only a factor of 3-4. The gross dependence of the magnetostriction on \( T \) and \( H \) is thus given fairly well even by the MFA in which \( (\Delta \mathcal{L}/\mathcal{L}) \approx \text{const.} \times \sigma^2 \).

The prediction of the precise \( T \) dependence of the \( \left( \frac{\Delta \mathcal{L}}{\mathcal{L}} / \sigma^2 \right)_0 \) curve by any model is a much more stringent test of that model's handling of the two-spin correlations than is the prediction of \( \left( \frac{\Delta \mathcal{L}}{\mathcal{L}} / H^2 \right)_0 \). The MFA is poor because it ignores the short-range correlations. The high temperature series method is much better because it includes (in principle) all the short-range correlations.

If the magnetostriction was a pure isotropic volume contraction, then the \( \mathbf{H} \parallel \mathcal{L} \) and \( \mathbf{H} \perp \mathcal{L} \) data would have been identical. Comparing the experimental results for the two configurations, we see that at high \( T \), the values for \( \left( \frac{\Delta \mathcal{L}}{\mathcal{L}} / \sigma^2 \right)_0 \) were
essentially the same (with some scatter, within the experimental errors). Near $T_C$, however, there is a difference of approximately 25%. This difference may be due to: 1) experimental errors which are $\leq 10\%$ for either configuration; 2) inaccuracies in the calculation of the demagnetizing corrections (see the discussion in Chapter III); or 3) actual orientation-dependent terms in the magnetostriction, either form effects or an intrinsic anisotropic magnetostriction such as might arise from a strain-dependent anisotropy energy.

To investigate the possible orientation-dependent contributions to the magnetostriction, the magnetostriction at 4.2 K was measured. At this temperature, the spin system was almost completely saturated within each domain. The application of a magnetic field (with magnitude $\sim 2N_\mathbf{S}$) then caused the processes of domain growth and domain rotation to take place. There would be very little change in the exchange energy during such an experiment, and hence very little exchange magnetostriction. Any magnetostrictive effects seen were then mostly due to changes in the anisotropy energy and the magnetostatic energy—i.e., due to orientation-dependent terms in the magnetostriction.

The total change in length along the $[001]$ axis due to these orientation-dependent terms was measured with $\mathbf{H} \parallel [001]$ and $\mathbf{H} \parallel [010]$. For both cases, $(\Delta l / l)$ due to the orientation-dependent effect was less than 5% of $\frac{1}{3}(\nu_1 + \nu_2)$—the scale factor for the exchange magnetostriction. It therefore seems
unreasonable to attribute all of the 25% difference between the values of \( \left\{ \frac{\Delta l}{l} / \sigma^2 \right\}_0 \) for \( \hat{H} \parallel \hat{z} \) and \( \hat{H} \perp \hat{z} \) to this source, although it may account for some of the difference, as follows.

The dependence on \( \sigma \) of the anisotropic magnetostriction and form effect may differ from that of the exchange magnetostriction, and thus the \( \sigma \rightarrow 0 \) limiting slopes may be affected to a larger degree. The exchange magnetostriction is approximately proportional to \( \left\{ \sum_n v_n A_n(0,T) \right\} \times \sigma^2 \). On the other hand, the anisotropy and form terms are approximately proportional to \( \sigma^2 \) (without the \( v_n A_n(0,T) \) factors). Hence, the orientation-dependent contribution to the slopes \( \left\{ \frac{\Delta l}{l} / \sigma^2 \right\}_0 \) may be emphasized by a factor \( \approx l/A_n(0,T)^{\geq 3} \) at the lowest \( T \), so that differences of order \( \approx 10\% \) between the data for \( \hat{H} \parallel \hat{z} \) and \( \hat{H} \perp \hat{z} \) may be expected near \( T_C \). It must be emphasized that the qualitative features of the \( \left\{ \frac{\Delta l}{l} / \sigma^2 \right\}_0 \) vs \( T \) curves would not be significantly altered by these effects.

In conclusion of this discussion, the differences in \( \left\{ \frac{\Delta l}{l} / \sigma^2 \right\}_0 \) for the \( \hat{H} \parallel \hat{z} \) and \( \hat{H} \perp \hat{z} \) configurations do not seem to be particularly significant. For the purposes of further comparisons with theory, we shall form the combination

\[
\left\{ \frac{\Delta l}{l} / \sigma^2 \right\}_0 \equiv \left\{ \frac{\Delta l}{l} / \sigma^2 \right\}_0, \hat{H} \parallel \hat{z} + 2 \left\{ \frac{\Delta l}{l} / \sigma^2 \right\}_0, \hat{H} \perp \hat{z} .
\]

(VII.8)

For this combination, the contribution of the anisotropic magnetostriction (but not of the form effect) is theoretically zero. This combination represents our best estimate for the
volume magnetostriction in EuS and it will be compared with the theoretical calculations of \( \Delta V/V \) in the preceding chapter.

The Parameters \( v_n \)

According to the theory presented in Chapter VI, there is a contribution to the volume magnetostriction coming from the \( P \) dependence of each of the exchange constants \( J_n \). The major results are embodied in the equation

\[
\frac{V(H) - V(O)}{V(O)} = \sum_n v_n \Delta n_n(H,T) = \left[ \sum_n v_n A_n(H,T) \right] c^2(H,T) . \quad \text{(VII.9)}
\]

The magnetoelastic coupling is contained in the parameters \( v_n \), given by

\[
v_n = -S^2 N z_n \left( \frac{\partial J_n}{\partial P} \right)_T . \quad \text{(VII.10)}
\]

In EuS, only the nearest- and next-nearest-neighbor exchange constants are believed to be important, so that one expects that only \( v_1 \) and \( v_2 \) will give a significant contribution to \( \Delta V/V \). There have been no direct measurements of the two \( v_n \) (i.e., no measurements of the \( P \) dependence of \( J_1 \) and \( J_2 \)) for EuS. Below, we present two ways of determining the \( v_n \) (or more correctly, certain weighted sums of the \( v_n \)) from available experimental data.

First, the \( P \)-dependence of \( T_C \) is related to the \( P \) dependence of the \( J_n \). According to the MFA, for a ferromagnet with two exchange constants, \( T_C \) is proportional to \( (z_1 J_1 + z_2 J_2) \).
More exact theories indicate, however, that the proportionality "constant" between $T_C$ and $(z_1J_1 + z_2J_2)$ is a function of $\alpha = J_1 / J_2$. This "constant" may be estimated from analyses of high temperature series expansions by procedures such as in ref. (15). We have performed such analyses. It then becomes possible to write an equation of the form

$$\frac{\partial (kT_C)}{\partial P} = k_1 \left( \frac{\partial J_1}{\partial P} \right) + k_2 \left( \frac{\partial J_2}{\partial P} \right),$$

(VII.11)

where the $k_1$ and $k_2$ are (functions of $\alpha$) obtained from such analyses and $k$ is the Boltzmann constant. For EuS ($\alpha = -0.45$), $k_1 = 104.0 \pm 4.0$ and $k_2 = 80.3 \pm 8.0$. When $\alpha = 0$ (i.e., $J_2 = 0$), but allowing for the possibility of a $P$-dependent $J_2$, then $k_1 = 99.3 \pm 1.0$ and $k_2 = 66.5 \pm 5.0$. Combining Eqs (VII.10) and (VII.11), we obtain

$$k_1 \nu_1 + k_2 \frac{Z_1}{Z_2} \nu_2 = -S^2 \frac{N}{V} z_1 k \left( \frac{\partial T_C}{\partial P} \right).$$

(VII.12)

The $P$ dependence of $T_C$ for EuS has been measured\(^{(16,17)}\) and found to be $[\partial T_C / \partial P] = -0.28 \pm 0.01$ K/kbar. Thus the right-hand-side of Eq. (VII.12) may be evaluated.

The second way of determining the $\nu_n$ is from the magnetic part of the thermal expansion. As discussed in Chapter VI, when the sample is cooled from $T = \infty$ to $T = 0$ at $H = 0$, the magnetoelastic interactions cause a fractional change in volume
\[
\frac{V(T=\infty)-V(0)}{V(\infty)} \equiv \left[ \frac{\Delta V}{V} \right]_{\text{tot}} = \sum_n \nu_n = (\nu_1+\nu_2). \tag{VII.13}
\]

From x-ray measurements of the lattice parameter, \(^{(11)}\)
\[
[\Delta V/V]_{\text{tot}} = -(1.2 \pm 0.3) \times 10^{-3},
\]
where only the magnetic contribution to the volume change was included. A value for the volume reduction during the cooling was also obtained in the present experiments. The sample was started at \(T=4.2\) K (using a Helium bath). The Helium was boiled off, and the change in length of the sample monitored as the sample warmed up. Curves similar to Fig. (VII.7) were traced out. By analyzing such curves, the change in the sample's length along the [001] direction between 4.2 K and \(\sim 35\) K could be determined. To obtain \((\Delta \ell/\ell)_{\text{tot}}\), this number was corrected in two ways: 1) in a separate experiment, by pumping on the Helium bath, the contraction between \(T=4.2\) K and \(\sim 1.8\) K was measured—any further contraction between 1.8 K and 0 K was ignored; and 2) to extrapolate to \(T=\infty\) from \(T=35\) K, Eq. (VI.11) was used to write

\[
\frac{\ell(T)-\ell(0)}{\ell(0)} = \sum_n \frac{1}{3} \nu_n \left[ \eta_n(T) - \eta_n(0) \right] \tag{VII.14}
\]

At \(T\sim 35\) K, we expect \(\eta_1\) and \(\eta_2\) to be small and when \(|\nu_1| < |\nu_2|\)

\[
\frac{\ell(T)-\ell(0)}{\ell(0)} \sim \sum_n \frac{1}{3} \nu_n \left[ \eta_1(T) - 1 \right] = \left[ \frac{\Delta \ell}{\ell} \right]_{\text{tot}} \left[ 1 - \eta_1(T) \right]. \tag{VII.15}
\]
Fig. (VII.7). The elongation $\frac{\Delta l}{l} \propto C$ of an EuS sample as it is warmed from $T=4.2$ K. The total elongation between $4.2$ K and $\sim 35$ K amounts to about $\frac{\Delta l}{l} = 340 \times 10^{-6}$. 

EuS, $l \parallel [001]$
High temperature series for the free energy are available for a single exchange constant model (see Table (VI.1)). From these series, it is possible to calculate $\eta_1(T/T_C)$. In particular, $\eta_1(T/T_C=2)=0.07$. Assuming this value is also valid for EuS, and using Eq. (VII.15), the change in length between $T=0$ and $T=\infty$ was then estimated. The conclusion is that in a cooling process, the fractional change in volume is $(AV/V)_{\text{tot}}=-(1.13 \pm 0.15) \times 10^{-3}$. The approximation used to obtain Eq. (VII.15) from Eq. (VII.14) is strictly valid only if $\eta_1(T)=\eta_2(T)$. In fact, we expect that $0.07\eta_1(2T_C)/\eta_2(2T_C)>0$. Even if $\eta_1=\eta_2$, setting $\eta_2(2T_C)=0.07$ will give at most an error of $\sim 3\%$ in $(AV/V)_{\text{tot}}$.

A value for $\nu_{\text{tot}}$ may also be obtained from the magnetostriction data itself. At high temperatures, $\chi_1(H,T)\approx\chi_2(H,T)\approx 1$. The magnetostriction, as given by Eq. (VII.9), is then

$$\frac{\Delta \ell}{\ell} \approx \sum_n \frac{1}{3} \nu_n \sigma^2 = \frac{1}{3} \nu_{\text{tot}} \sigma^2 .$$  \hspace{1cm} (VII.16)

The initial slope of the $\Delta \ell/\ell$ vs $\sigma^2$ curves have been obtained from the present experimental data. These slopes imply that

$$\left[\frac{\Delta V}{V}\sigma^2\right]_0=-(1.09 \pm 0.10) \times 10^{-3} \text{ for } 5\% T/T_C<9. \text{ The High Temperature Series for } \alpha=-0.45 \text{ predict that in this temperature range, } A_1=0.95 \pm 0.02 \text{ and } A_2=1.01 \pm 0.01. \text{ Taking these values into account, the high T magnetostriction data predicts } \nu_{\text{tot}}=-(1.11 \pm 0.13) \times 10^{-3}, \text{ in good agreement with values obtained from the thermal expansion data.}$$
In principle, Eqs. (VII.12) and (VII.13) can now be solved to obtain \( v_1 \) and \( v_2 \). (The solution, for \( \alpha = -0.45 \), is \( v_1 = -(1.30 \pm 0.50) \times 10^{-3} \) and \( v_2 = (0.17 \pm 0.36) \times 10^{-3} \).) However, the uncertainties in the values for \( \partial T_C / \partial P \) and \( (\Delta V / V)_{\text{tot}} \) make the usefulness of such a procedure questionable. Nonetheless, the solution suggests that the magnetostriction is largely due to the \( v_1 \) term (i.e., the P dependence of \( J_1 \) seems to be stronger than that of \( J_2 \)).

Another way of dealing with Eqs. (VII.12) and (VII.13) is to assume a value for the ratio \( R = \frac{\partial J_2}{\partial P} / \frac{\partial J_1}{\partial P} \) (and hence the ratio \( v_2 / v_1 = R z_2 / z_1 \)). The measurements of \( \partial T_C / \partial P \) and \( (\Delta V / V)_{\text{tot}} \) are then treated as alternative independent methods for the determination of \( v_1 \) and \( v_2 \). Consider the quantity \( v_{\text{tot}} = (v_1 + v_2) \). According to Eq. (VII.13), \( v_{\text{tot}} = (\Delta V / V)_{\text{tot}} \) independent of the value of \( R \). Once \( R \) has been specified, we can also obtain a value for \( v_{\text{tot}} \) from the measured \( \partial T_C / \partial P \). For EuS, Eq. (VII.12) may be rewritten as

\[
v_{\text{tot}} = -(1.04 \pm 0.07) \times 10^{-3} \frac{1+0.5R}{1+(0.77 \pm 0.04)R}.
\]

This expression is not strongly \( R \) dependent for \( R \leq 0 \). The large uncertainties in the simultaneous solution of Eqs. (VII.12) and (VII.13) are due to the mildness of this \( R \) dependence.

Unfortunately, there is no exact procedure for estimating \( R \), but we can investigate a number of different assumptions, which are more or less reasonable: 1) if the magnetoelastic coupling is entirely due to \( J_1 \), then \( R = 0 \) and
from Eq. (VII.15) \( \nu_{\text{tot}} = -(1.04 \pm 0.07) \times 10^{-3} \). This value is in rough agreement with the thermal expansion data; 2) Alternatively, if the \( P \) dependence of \( J_2 \) dominates, and \( R = \infty \), then \( \nu_{\text{tot}} = -(0.68 \pm 0.1) \times 10^{-3} \), in clear disagreement with the thermal expansion data. This is not surprising because it is reasonable that the \( P \) dependence of \( J_2 \) (the "minor" exchange constant) is weaker than the \( P \) dependence of \( J_1 \) (the "major" exchange constant); 3) the most recent plots of the exchange constants \( J_1 \) and \( J_2 \) versus the lattice constant \( a_0 \) in the Europium Chalcogenides\(^8\) indicate that \( \frac{\partial J_1}{\partial a_0} \gtrsim \frac{\partial J_2}{\partial a_0} \). It is, however, far from certain that the ratio \( R \) obtained from such plots is applicable to \( \text{EuS} \). Indeed, measurements of the magnetic Gruneisen constant \( \gamma_m = \frac{\partial \ln J_1}{\partial \ln V} = -5.3 \) in \( \text{EuO}\(^{18}\) \) do not agree with \( \left( \frac{\partial \ln J_1}{\partial \ln a_0^3} \right)^2 = 1 \) taken from the \( J_1 \) vs \( a_0 \) plot. Nevertheless, if we take the ratio \( R \) from the plot of \( J_1 \) and \( J_2 \) vs \( a_0 \), then \( R = 1 \) and from Eq. (VII.15), \( \nu_{\text{tot}} = -(0.88 \pm 0.08) \times 10^{-3} \); 4) another assumption that we might make is that \( \alpha = J_2 / J_1 \) remains constant when \( P \) is applied. This means that \( R = \alpha = -0.45 \) for \( \text{EuS} \). Hence, from Eq. (VII.15), \( \nu_{\text{tot}} = -(1.23 \pm 0.12) \times 10^{-3} \), which is consistent with the thermal expansion data.

There is no definite way to chose any particular value for \( R \). Intuitively, we expect that \( |\nu_1| \gtrsim |\nu_2| \).

We thus conclude that measurements performed on our \( \text{EuS} \) sample suggest that the value \( \nu_{\text{tot}} = -(1.12 \pm 0.14) \times 10^{-3} \) be adopted. This number is in good agreement with the previous (albeit less accurate) measurements of the thermal expansion.
It is also in good agreement with measurements of $\partial T_C/\partial P$ as long as the ratio $R = \frac{\partial J_2}{\partial P}/\frac{\partial J_1}{\partial P}$ is not too large (essentially, $|R| \lesssim 0.5$). We have no definite procedure for choosing a particular value for $R$, except for the expectation that $|R| \lesssim 0.5$ (or equivalently, $|v_2/v_1| \lesssim 1$). We will see later, however, that the theoretical predictions for $\left(\frac{\Delta V}{V}/\sigma^2\right)_0$ are not very sensitive to the value of $R$. As a consequence, the lack of a definite value of $R$ is not a severe limitation to the comparison of theory with experiment.

**Comparison with Theory**

We are now in a position to compare the experimentally measured values for $\left(\frac{\Delta V}{V}/\sigma^2\right)_0$ with the theory presented in Chapter VI. The calculations in that chapter focused mainly on two separate aspects of the theory. The first was the relation of the magnetostriction to certain thermodynamic properties of the system ($\eta_n(H,T)$ or $\sigma(H,T)$ and $A_n(H,T)$) and the coupling constants (the $v_n$). The second aspect involved the calculation of these functions using the method of High Temperature Series Expansions for a particular choice of model system (the isotropic Heisenberg model with two exchange constants). There are a variety of ways to proceed in comparing theory with experiment. The method utilized here is to compare the quantity $\left(\frac{\Delta V}{V}/\sigma^2\right)_0$ with that calculated from the model. Such a procedure makes use of experimentally determined values of $\sigma(H,T)$ or $\bar{\chi}(H,T)$, rather than values calculated theoretically. The quantities $\sigma$ and $\bar{\chi}$ are affected.
to a large degree by the presence of long-range interactions (such as dipole-dipole interactions). It is difficult to take the effect of these interactions completely into account in a theoretical calculation. These difficulties are avoided by using the experimental quantities.

For example, we consider the susceptibility $\chi (T)$. Fig. (VII.8) shows the values of $\chi (T)$ obtained from the measured $\sigma (H,T)$ and the values calculated by the method of High Temperature Series. In this comparison there are no adjustable parameters. The agreement is fairly good, but when looked at more closely, discrepancies become apparent. Fig. (VII.9) shows the ratio of the measured and calculated susceptibilities, $\chi_0 (\text{meas})/\chi_0 (\text{calc})$, as a function of temperature. As can be seen, the calculation consistently overestimates $\chi_0$, the discrepancy becoming more and more pronounced as $T \to T_C$. The functions $A_n$ are calculated using these same series. However, the $A_n$ are much less sensitive to the details of the model than is $\chi$ (see, for example, Fig. (VI.3) which contrasts the $A_1$ values for different choices of $\alpha = J_2/J_1$). Hopefully, then, the comparison of $\left( \frac{\Delta V}{V} / \sigma^2 \right)_0$ with theory will not be too much in disagreement.

The values for $\left( \frac{\Delta V}{V} / \sigma^2 \right)_0$ obtained by combining the results of the longitudinal and transverse magnetostrictions are plotted in Fig. (VII.10). The figure shows only the low temperature data ($1<T/T_C<1.2$), close to $T_C$. Also shown are a
Fig. (VII.8). The T-dependence of the reduced zero-field susceptibility in EuS. The solid curve is calculated for the S=7/2 Heisenberg ferromagnet with two exchange constants and α=-0.45 (appropriate to EuS).
Fig. (VII.9). The variation with \( T \) of the ratio of the measured and predicted (from high-temperature series calculations) values of the reduced susceptibility.
Fig. (VII.10). The $T$-dependence of $\left[ (\Delta V/V)/\sigma^2 \right]_0$ near $T_C$. The solid curves are calculated from Eq. (VII.17) for a variety of values of $R=\frac{3J_2}{2P}\frac{3J_1}{2P}$. All the curves are drawn assuming a value of $v_{tot}=-1.12 \times 10^{-3}$. 
family of theoretical curves. To draw these curves, Eq. (VI.20) has been used, in the form

\[
\left( \frac{\Delta V}{V} / \sigma^2 \right)_0 = v_1 A_1(H=0,T) + v_2 A_2(H=0,T).
\]  

(VII.17)

The values for \( v_1 \) and \( v_2 \) were chosen as in the previous discussion, so that several curves could be drawn depending on the particular choice of the parameter \( R \). (For all these curves, \( v_{\text{tot}} = v_1 + v_2 = -1.12 \times 10^{-3} \).) The \( A_n(H=0,T) \) were calculated from the High Temperature Series parameterized relevant to EuS.

The general features of all the theoretical curves are the same. They match the high \( T \) (\( T < 4T \)) data points (not plotted in this figure, but see Fig. (VII.6)) reasonably well, and dip towards zero as \( T \) decreases towards \( T_C \), just as the experimental points do. Because \( A_1 \) and \( A_2 \) do not differ by very much (as for example in Fig. (VI.4)), the effect of varying \( R \) does not shift the theoretical curves excessively, and any of the family of curves could be said to agree fairly well with the experimental data. The uncertainty in the value of \( R \) which should be adopted makes any quantitative discussion of the discrepancies between theory and experiment difficult.

We remark, however, that the theoretical curves for \( |R| < 1 \) (an inequality which we expect to be true) seem to consistently underestimate the magnitude of \( \left[ (\Delta \xi / \xi) / \sigma^2 \right]_0 \). Similar discrepancies are seen in the comparison of the
experimental and theoretical curves of $\bar{X}_0$, and may probably be traced to the same cause—the critical properties (i.e., the behavior as $T \to T_C$) of EuS are not precisely as predicted by the Heisenberg model, due, at least in part, to the effect of the dipole-dipole forces. (19)

In summation of this discussion, we remark that the Mean Field Approximation gives a very poor description of the $\left[\frac{\Delta V}{V}/\sigma^2\right]_0$ data. According to the MFA, $\left[\frac{\Delta V}{V}/\sigma^2\right]_0 = v_{\text{tot}} = -1.12 \times 10^{-3}$, a constant, independent of temperature. The experimental data exhibit increasingly large disagreements with the MFA prediction as $T$ is lowered towards $T_C$. On the other hand, the high-temperature-series expansions, while they do not seem to give excellent agreement, do provide a good qualitative description of the $\left[\frac{\Delta V}{V}/\sigma^2\right]_0$ measurements.

Magnetostriction in Strong Magnetic Fields

Up to this point, the discussion has been mainly concerned with the magnetostriction at sufficiently low $H$ that no large alignment of the magnetic moments took place (essentially, $\sigma \approx 0.15$). The $H=0$ asymptotes of $\left[\frac{\Delta L}{L}/\sigma^2\right]$ have been compared with model calculations, and a simple estimate of the deviations from the $H=0$ behavior at low $H$ was presented. We now turn to the high magnetic field limit, when the magnetic moment approaches saturation.

Fig. (VII.11) shows the longitudinal magnetostriction at $T=17.04$ K measured in fields up to $H_{\text{int}} \approx 130$ kOe. There is a
Fig. (VII.11). The longitudinal magnetostriction measured at $T=17.04$ K, a temperature close to $T_C$. 

$10^6 \Delta l/l$ vs $H$ (kOe)

$\text{EuS, } \vec{H} \parallel \vec{e}$

$T=17.04$ K
rapid onset in the magnetostriction which levels off as the
spin system approaches saturation. (At the highest fields in
the figure, $\sigma=0.95$.) If the ratio $\left(\frac{\Delta L}{L}/\sigma^2\right)$ is formed, a
behavior as in Fig. (VII.12) is obtained. In this figure, the
values of $\left(\frac{\Delta L}{L}/\sigma^2\right)$ for both the longitudinal and transverse
configurations are shown, plotted against $\sigma$. As $\sigma$ increases,
there is a gradual increase in the magnitude of $\left(\frac{\Delta L}{L}/\sigma^2\right)$.

According to the magnetostriction theory, $\left(\frac{\Delta L}{L}/\sigma^2\right)$ is
given by

$$\left(\frac{\Delta L}{L}/\sigma^2\right) = \nu_1 A_1(H,T) + \nu_2 A_2(H,T).$$  \hspace{1cm} (VII.18)

The $A_n$ can be calculated only in the limit $H\to 0$, for the two-
exchange-constant model. In addition, for the single-exchange-
constant model, High Temperature Series are available which
allow the calculation of $A_1(H,T)$ for small $H$ (as discussed in
connection with Figs. (VII.2) and (VII.3)) and for the $H=\infty$
limit, $A_1(H=\infty,T)$ (as in Fig. (VI.5)). The experimental curves
follow our expectation that $\left(\frac{\Delta L}{L}/\sigma^2\right)$ increases in magnitude
smoothly from its $H=0$ value to the $H=\infty$ value as the field is
increased. Numerical comparisons are difficult since the
needed series for two exchange constants are not available.

A simple estimate of the $H=\infty$ (i.e., $\sigma+1$) intercept of
$\left(\frac{\Delta L}{L}/\sigma^2\right)$ is indicated in the figure by an arrow. The estimate
was formed by writing, for $\alpha=-0.45$ (appropriate for EuS)
Fig. (VII.12). The variation of the ratio $\frac{\Delta l}{l}/\sigma^2$ with $\sigma$ for the longitudinal ($\hat{H} || \hat{z} || [001]$) and transverse ($\hat{H} || \hat{z} || [001]$) configurations. The arrow indicates an estimate of the $\sigma=1$ limit calculated from Eq. (VII.21).
Here, $V_{tot} = -1.12 \times 10^{-3}$, the number developed for EuS. Unfortunately, the high-temperature series needed to calculate $A_1(\infty, T; \alpha)$ are available only for the single-exchange-constant model (i.e., $\alpha=0$). For $T/T_C = 1.036$ (the same $T/T_C$ as in Fig. (VII.12)), these series give $A_1(\infty, T; \alpha=0) \approx 0.77$. However, even at $H=0$, the models of $\alpha=0$ and $\alpha=-0.45$ give different results. For $T/T_C = 1.036$, we have, as $H \to 0$,

$$A_1(0, T; \alpha=-0.45) \approx 0.73$$  \hspace{1cm} (VII.20)

To take this difference into account, we write the approximation

$$A_1(\infty, T; \alpha=-0.45) \approx \frac{A_1(0, T; \alpha=-0.45)}{A_1(0, T; \alpha=0)} A_1(\infty, T; \alpha=0) \hspace{1cm} (VII.21)$$

The final result is $\left[\frac{\Delta k}{\xi^2}\right]_{H \to \infty} \approx -210 \times 10^{-6}$, as indicated in Fig. (VII.12). The agreement of this estimate with the experimental asymptote is fairly good. It underestimates the $H \to \infty$ limit of $\left[\frac{\Delta k}{\xi^2}\right]$ by about 14%, but all our theoretical curves (for reasonable values of $R$) also underestimate the $H \to 0$ limit.

**Conclusions**

The linear magnetostriction of EuS for the configurations $\mathbf{H} || [\mathbf{100}]$ and $[010] || \mathbf{H} || [001]$ was measured over a temperature range $1.02 T_C \leq T \leq 9 T_C$, in magnetic fields up to
140 kOe. The volume magnetostriction was deduced from the measured linear magnetostrictions.

The analysis of the data and the comparison with the theory presented in Chapter VI lead to the following conclusions: 1) The dominant contribution to the magnetostriction above \( T_C \) is an isotropic volume magnetostriction which has its origin in the dependence of the exchange energy on the volume of the sample. 2) The theory of Callen and Callen,\(^{(20)}\) or the treatment which leads to Eq. (VI.20), which gives equivalent results, gives a fairly good description of the isotropic magnetostriction and its relation to the \( H \)-induced changes in the two-spin correlation functions. 3) The model of a Heisenberg ferromagnet with two exchange constants (between nearest neighbors and next-nearest neighbors) is reasonably good for a quantitative description of the data. Deviations near \( T_C \), however, in both the magnetostriction and magnetization data, suggest that this model is not exact. 4) Analysis of the magnetostriction and magnetization data at low and intermediate fields demonstrate the usefulness of high temperature series expansions.
REFERENCES

6 See also: W. Zinn (Ref. 8) who quotes, as an average for many experimenters, $J_1/k=0.21 \pm 0.03$ K and $J_2/k=-0.11 \pm 0.01$ K; and L. Passelli, et al., Phys. Rev. 14, 4897 (1976), who measure $J_1/k=0.236 \pm 0.009$ K and $J_2/k=-0.118 \pm 0.011$ K in neutron scattering experiments.
8 W. Zinn, JMMM 3, 23 (1976).

