Stress Dependence and the Latent Heat of the Morin Transition in Fe$_2$O$_3$[†]

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Existing data on the magnetoelastic interaction, elastic constants, and magnetic anisotropy are used to calculate, as a function of temperature, the value of hydrostatic pressure or uniaxial stress required to induce spin flop in Fe$_2$O$_3$. The results are in good qualitative agreement and fair quantitative agreement with existing data. The latent heat of the Morin transition is also calculated using these data, and the result suggests that the Morin transition is driven by an entropy difference.

I. INTRODUCTION

Recently, evidence has been presented[1] that uniaxial stress induces spin flop in the antiferromagnet Cr$_2$O$_3$, and a detailed phenomenological analysis of the effect has been made.[2] The Cr$_2$O$_3$ analysis can be extended to Fe$_2$O$_3$, which has the same symmetry properties as Cr$_2$O$_3$ and appears to be an attractive candidate for studying stress-induced spin flop. Fe$_2$O$_3$ has the corundum structure and orders magnetically at $T_N = 947$ K. For temperatures between T_N and the Morin temperature T_M = 261 K, Fe$_2$O$_3$ is a canted antiferromagnetic (weak ferromagnet) with the spins perpendicular to the c axis except for slight canting out of the basal plane. For temperatures below T_M, Fe$_2$O$_3$ is a uniaxial antiferromagnet with the spins lying along the c axis.[3] The transition at T_M is commonly called the Morin transition, after its discoverer. This transition can be described by a phenomenological thermodynamic theory due originally to Dzialoshinsky[4] and modified slightly by others to accommodate new experimental data. In the most recent treatment, due to Ozhogin and Shapiro,[5] the condition for the Morin transition is found to be

$$f(T_M) = a_1 + \tfrac{1}{2} a_2 - \beta^2/B = 0 , \qquad (1)$$

where the temperature-dependent quantities a_1, a_2, β, and B are defined by their appearance as coefficients of terms in the phenomenological magnetic free energy $\mathfrak{F}$ as follows:

$$\mathfrak{F} = M \big[\tfrac{1}{2} B(m_x^2 + m_y^2 + m_z^2) + \tfrac{1}{2} a_1(l_x^2 + l_y^2) $$
$$- \beta(m_x l_y - m_y l_x) - (\tfrac{1}{4} a_2) l_z^4 \big] . \qquad (2)$$

In Eq. (2) M is the saturation sublattice magnetization, and m_i and l_i are the direction cosines of the sum and difference of the sublattice magnetizations, respectively. The analysis of Ozhogin and Shapiro includes other terms in the magnetic free energy, but these are not relevant here and have been excluded.

Evidently a study of stress-induced spin flop in Fe$_2$O$_3$ is essentially a study of the stress dependence of T_M. From Eq. (1) this entails the stress dependence of a_1, a_2, β, and B. It is shown later that the stress dependence of a_1 and a_2, the anisotropy constants, is the most important of these. Recently, the constants of the magnetoelastic interaction, second order in the l_i and first order in the crystal strains ϵ_i, have been experimentally determined from magnetostriction measurements.[6] The elastic constants of Fe$_2$O$_3$ are also known.[7] From this information can be deduced the stress dependence of a_1 and the size of other stress-induced anisotropies second order in the l_i. It is the purpose of this paper to explore quantitatively for the temperature range 0–300 K, the stress dependence of T_M that can be deduced from the information at hand. The analysis is hampered primarily by incomplete information about the temperature dependence of a_1 and a_2, which is known accurately only for temperatures below T_M, and by uncertainties about the stress dependence of a_2.

Previous work in this area includes experimental studies showing that compressive hydrostatic pressure causes T_M to increase,[8-11] and a phenomenological analysis of this effect by Pakhomov.[12] However, Pakhomov's work preceded the determination of the magnetoelastic interaction constants and thus could not be quantitative. Also, his analysis dealt only with the effects of hydrostatic pressure.

The latent heat of the Morin transition can also be obtained from the data used in the magnetoelastic analysis, and this is done in Sec. IV. The implications of the result obtained are discussed there briefly.

II. STRESS DEPENDENCE OF T_M

A. Magnetoelastic Interaction

The magnetoelastic free energy is written in Voigt's notation as

$$\mathfrak{F}_{me} = \sum_{ij} \epsilon_i F_{ij} l_i . \qquad (3)$$

F_{ij} is the matrix of magnetoelastic coefficients, and for crystals with the symmetry of Cr$_2$O$_3$ and

Fe_2O_3 it has the nonzero elements,[2] $F_{11} = F_{22}$, F_{12}
$= F_{21}$, $F_{13} = F_{32}$, $F_{14} = -F_{24} = F_{65}$, $F_{41} = -F_{42} = F_{56}$,
F_{33}, $F_{44} = F_{55}$, $F_{66} = F_{11} - F_{12}$. This is the general
form of the interaction employed in the Cr_2O_3 analy-
sis. The form employed by Levitin, Pakhomov,
and Shchurov[6] in analyzing their magnetostriction
measurements is a special one that can be obtained
from the form above by subtracting a term iso-
tropic in the l_i, which is

$$\{F_{13}(\epsilon_{xx} + \epsilon_{yy}) + F_{31}\epsilon_{zz}\} (l_x^2 + l_y^2 + l_z^2) \ . \tag{4}$$

Such a subtraction has no effect on the analysis of
physical quantities sensitive only to anisotropy.[2]
Comparing the form thus obtained with that of Lev-
itin, Pakhomov, and Shchurov yields the following
correspondence between their coefficients δ_i and
the F_{ij} above:

$$F_{11} + F_{12} - 2F_{13} = \delta_1 + \delta_2 = -3.2 \times 10^7 \text{ erg/cm}^3 \ ,$$

$$F_{11} - F_{12} = \delta_1 - \delta_2 = 1.7 \times 10^7 \text{ erg/cm}^3 \ ,$$

$$F_{33} - F_{31} = \delta_3 = -.39 \times 10^7 \text{ erg/cm}^3 \ , \tag{5}$$

$$4F_{44} = \delta_4 = 7.8 \times 10^7 \text{ erg/cm}^3 \ ,$$

$$2F_{14} = \delta_5 = 5.6 \times 10^7 \text{ erg/cm}^3 \ ,$$

$$2F_{41} = \delta_6 = 3.7 \times 10^7 \text{ erg/cm}^3 \ .$$

These values were found to be independent of tem-
perature within experimental error in the range
of measurement, 100–300 K, and here will be as-
sumed independent of temperature in the range
0–300 K.

B. Hydrostatic Pressure or c Axis Uniaxial Stress

Analyzing the effect of stress that preserves the
crystal symmetry is the most straightforward.
Letting P be the value of either uniaxial c-axis
stress or hydrostatic pressure, the value of P re-
quired to induce the Morin transition at any tem-
perature T, denoted $P_M(T)$, is given by

$$P_M(T) = -\frac{f(T)}{\partial f/\partial P} \ , \tag{6}$$

where $f(T)$ is defined in Eq. (1) and it is assumed
that only the linear dependence of $f(T)$ on P need be
taken into account. Evaluating Eq. (6) yields, for
$P_M(T)$, the expression

$$P_M(T) = -\left(a_1 + \tfrac{1}{2} a_2 - \frac{\beta^2}{B}\right) \Big/$$

$$\left(\frac{\partial a_1}{\partial P} + \frac{1}{2}\frac{\partial a_2}{\partial P} - 2\frac{\beta}{B}\frac{\partial \beta}{\partial P} + \frac{\beta^2}{B^2}\frac{\partial B}{\partial P}\right) \ . \tag{7}$$

The quantities B and β do not appear to be greatly
temperature dependent in the range 0–300 K and
their experimentally determined values are $\beta = 22.7$
kG,[5] and $B = 10\,590$ kG.[13] Thus the ratio β/B is
2.15×10^{-3} and the last two terms in the denomi-

nator of Eq. (7) are negligible unless B and β are
unusually stress dependent, which seems unlikely.
The quantity $\partial a_2/\partial P$ is not known, but it may be
significant that in the analysis of the magnetostric-
tion data for Fe_2O_3, mentioned in Sec. II A, it was
not necessary to include in the magnetoelastic in-
teraction terms fourth order in l_i. In this paper,
only the effects of $\partial a_1/\partial P$, which can be deduced
from existing information, will be included. The
validity of neglecting $\partial a_2/\partial P$ must be determined
ultimately by comparison of theory with experi-
ment. With these approximations $P_M(T)$ can be
written

$$P_M(T) = -\frac{K(T)}{\partial K_1/\partial P} \ , \tag{8}$$

where the energies K and K_1 are defined by

$$K \equiv \tfrac{1}{2}[(a_1 + \tfrac{1}{2} a_2) - \beta^2/B] (M) \ ,$$

$$K_1 \equiv \tfrac{1}{2} a_1 M \ , \tag{9}$$

and $M = 920$ emu/cm³ is the sublattice saturation
magnetization.[5,13]

In this section P is either a hydrostatic pressure
$P_{xx} = P_{yy} = P_{zz} = P$, or a uniaxial c-axis stress P_{zz},
where P_{ij} is the stress tensor. The analysis[2] for
Cr_2O_3 yielded the following formulas:

$$\frac{\partial K_1}{\partial P} = (F_{11} + F_{12} - 2F_{13})(S_{11} + S_{12} + S_{13})$$

$$+ (F_{31} - F_{33})(S_{33} + 2S_{13}) \ ,$$

$$\frac{\partial K_1}{\partial P_{zz}} = (F_{11} + F_{12} - 2F_{13})(S_{13})$$

$$+ (F_{31} - F_{33})(S_{33}) \ . \tag{10}$$

S_{ij} is the elastic compliance matrix and its values,
determined by inverting the known elastic constant
matrix,[7] are, in units of 10^{-12} cm²/dyn, $S_{11} = 0.44$,
$S_{12} = -0.103$, $S_{13} = -0.023$, $S_{14} = -0.083$, $S_{33} = 0.44$,
$S_{44} = 1.20$. Using these values, and those of Eq. (5)
to evaluate Eq. (10) gives

$$\frac{\partial K_1}{\partial P} = -0.71 \times 10^{-5} \ ,$$

$$\frac{\partial K_1}{\partial P_{zz}} = 0.25 \times 10^{-5} \ . \tag{11}$$

As mentioned at the end of Sec. II A above, the
F_{ij} (and presumably the S_{ij}) do not vary between 0
and 300 K, so it is consistent with experiment to
regard $\partial K_1/\partial P$ and $\partial K_1/\partial P_{zz}$ as temperature inde-
pendent in this temperature range. Although it may
at first seem strange that $K(T, P)$ is temperature
dependent while $\partial K/\partial P$ is not, there is no mathe-
matical inconsistency in this, and the experimental
data do imply that it is the case for T between 0
and 300 K.[14] Therefore the temperature depen-
dence of Eq. (8) is assumed to follow entirely from

the temperature dependence of $K(T)$, which, in the range 0–300 K where β and B are essentially constant, is due primarily to the temperature dependence of $a_1(T)$ and $a_2(T)$.

For temperatures less than T_M a magnetic field strength H_c applied along the crystal c axis induces spin flop. The formula for H_c that is given by Ozhogin and Shapiro[5] can be used to find the relation

$$K(T) = (M/2B)[H_c(T)]^2 , \tag{12}$$

and the data of Foner and Shapira[15] for $H_c(T)$ can then be used to find $K(T)$ for temperatures up to T_M, where K and H_c are zero. From antiferromagnetic-resonance measurements, Ozhogin and Shapiro have determined $a_1(T)$ and $a_2(T)$ in the range 0–220 K, and if their data, and the values of B and β given above, are used to evaluate Eq. (9) in this temperature range, the result is in good agreement with the $K(T)$ obtained from Eq. (12). In the range T_M to 300 K, the experimental results must be extrapolated in some way. The method employed here is somewhat arbitrary, but leads to a reasonable result and serves to point out the need for a better microscopic theory of $a_1(T)$ and $a_2(T)$ than is now available. Prior to the realization[16–18] that $a_2 \neq 0$, the Morin transition was assumed to occur approximately when the anisotropy energy $K_1(T)$ passed through zero. A value of K_1 at $T=0$ was determined from antiferromagnetic resonance experiments. Artman, Murphy, and Foner[19] assumed that K_1 was the sum of a single-ion contribution K_S and a magnetic dipolar contribution K_{MD}. They evaluated K_{MD} at $T=0$ and then deduced K_S at $T=0$. Using the molecular-field-approximation formulas
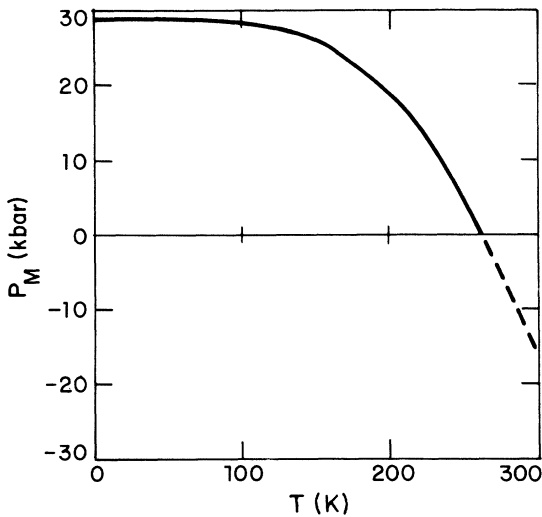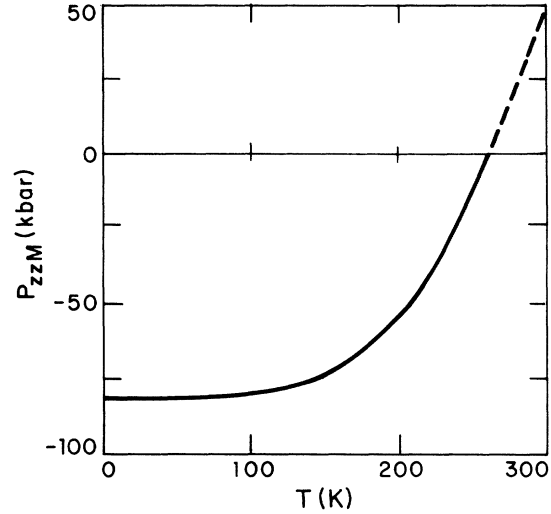

FIG. 2. Temperature dependence of the c-axis uniaxial stress required to induce spin flop. Dashed regions show extrapolation of existing data. Note that negative stress means compressive applied stress.

for the temperature dependence of K_S and K_{MD}, they evaluated $K_1(T)$ and found that their result passed through zero at 266 K, nearly T_M. The experimentally determined $K(T)$ for $T < T_M$ coincides quite closely with the calculated $K_1(T)$ curve except in the region near T_M. The slopes of the two curves are almost identical at their zero crossings. Therefore the calculated $K_1(T)$ curve has been used as a guide to extrapolate the experimental $K(T)$ curve from T_M to 300 K, but with the zero crossing being kept at T_M. Evidently, the calculated $K_1(T)$ gives a good account of $K(T)$, and inasmuch as the calculation was designed to produce only the temperature dependence of the anisotropy constant a_1 (for the anisotropy second order in the l_i), it is clear that the present theoretical understanding of $a_1(T)$ and $a_2(T)$ is inadequate. That a nonzero a_2 is required to explain the details of the antiferromagnetic-resonance data in Fe_2O_3 has been shown very clearly by Ozhogin and Shapiro.[5]

Combining Eqs. (8) and (11), and using the procedure just described to obtain $K(T)$, then yields the curves in Figs. 1 and 2, which show $P_M(T)$ and $P_{zzM}(T)$, respectively. Extrapolated regions are shown with a dashed line. Experimentally it is found that for compressive (negative) hydrostatic pressures up to at least 6 kbar, T_M increases linearly with P, the experimental value of $\partial T_M/\partial P_M$ being -3.7 ± 0.2 K/kbar.[9] Since the P_M-T_M curve is defined by setting K equal to zero, it is straightforward to find, for the assumptions made in this paper [see the discussion following Eq. (7)], that

FIG. 1. Temperature dependence of hydrostatic pressure required for spin flop. Dashed regions show extrapolation of existing data. Now that negative pressure means compressive applied pressure.

$$\frac{\partial T_M}{\partial P_M} = -\frac{\partial K/\partial P}{\partial K/\partial T} = -\frac{\partial K_1/\partial P}{\partial K/\partial T} . \tag{13}$$

From 240 K to T_M, Foner and Shapira[15] find that H_c^2 varies linearly with T such that $\partial(H_c^2)/\partial T = -6.3 \pm 0.2 \times 10^7$ G^2/K. From Eq. (12) it is then found that at T_M, $\partial K/\partial T = -2.74 \times 10^3$ erg/cm^3 K. Using this result with Eqs. (11) and (13) then gives the calculated $\partial T_M/\partial P_M$ at $P_M = 0$ to be -2.6 K/kbar, in good qualitative, but only fair quantitative, agreement with experiment. It seems most likely that the source of the discrepancy lies in the neglect of the stress dependence of a_2, suggesting that a more detailed determination of the magnetoelastic interaction is needed. It has also been reported that at 6 kbar of compressive hydrostatic pressure, $\partial T_M/\partial P_M$ changes rather suddenly to -1.0 ± 0.3 K/kbar.[10] To agree with this, the calculated curve of Fig. 1 would have to turn downward much more sharply in the region above 270 K. The source of this discrepancy may lie in the lack of knowledge of $K(T)$ in this region, in the neglect of $\partial a_2/\partial P$, or in the possibility that the magnetoelastic interaction is itself changing at higher pressures.

As Fig. 2 shows, the effect on T_M of a compressive (negative) uniaxial c-axis stress is opposite to that of compressive hydrostatic pressure, and $\partial T_M/\partial P_{zzM}$ at $P_{zz} = 0$ is found from Eq. (13) to be $+0.9$ K/kbar. There are no experimental results with which to compare the curve of Fig. 2. It would be desirable at least to confirm the prediction of a slope opposite to that for hydrostatic pressure. Although crystals shatter at much lower values of uniaxial stress than hydrostatic pressure, it should be possible at least to measure the change in T_M near $P_{zz} = 0$. It is perhaps worth noting that large uniaxial stress is rather easily and inexpensively generated.

C. Basal Plane Uniaxial Stress

Calculating the effect of stresses that alter the crystal symmetry is more difficult because new, lower symmetry magnetic anisotropies are generated by the stress. A detailed calculation[2] has been done for Cr$_2$O$_3$ where it appears that a_2 is zero and where there are no canting terms allowed in the free energy $\mathcal{F}(\beta = 0)$. Thus the Cr$_2$O$_3$ basal-plane calculation is not strictly applicable to Fe$_2$O$_3$. However, if the K of the Cr$_2$O$_3$ formulas is taken as the K of Eq. (9), the Cr$_2$O$_3$ results can be used to provide at least an indication of what might be expected in Fe$_2$O$_3$. It is found that for $T < T_M$, compressive basal-plane stress induces gradual spin rotation to a position nearly half-way between the c axis and the basal plane, but no abrupt flop to the basal plane. For $T > T_M$, the spins can be rotated gradually by compressive basal-plane stress to positions near the c axis, but again there is no abrupt flop. The magnitude of stress required is similar to those shown in Figs. 1 and 2. As any actual experimental data would have to be analyzed

in detail by the methods employed for Cr$_2$O$_3$, but including a_2 and β, it does not seem worthwhile to give any further details. There have been measurements[20] of the anisotropies induced in Fe$_2$O$_3$ by basal-plane stress and Pakhomov has shown these to be qualitatively in accord with the measured magnetoelastic interaction.[21]

III. LATENT HEAT OF MORIN TRANSITION

Since Dzialoshinsky's theoretical treatment,[4] there has been little attention paid to the latent heat L of the Morin transition. In particular, there does not appear to be either an experimental or a theoretical value for the latent heat. With the notation that 1 and 2 label the magnetic state below and above T_M, respectively, and using the assumptions stated in Sec. II, the latent heat of the transition from 1 to 2 is obtained as

$$L(1 \to 2) = T_M [S_2(T_M) - S_1(T_M)]$$
$$= -T_M \left(\frac{\partial[\mathcal{F}_2 - \mathcal{F}_1]}{\partial T}\right)_{T_M}$$
$$= -T_M \left(\frac{\partial K}{\partial T}\right)_{T_M}, \tag{14}$$

where S is the entropy. Combining Eqs. (13) and (14) then gives

$$L = T_M \left(\frac{\partial K_1}{\partial P}\right)_{T_M} \Big/ \left(\frac{\partial T_M}{\partial P_M}\right)_{T_M}. \tag{15}$$

It is interesting to see that this result is essentially the Clausius-Clapeyron equation[22] for L. From the results of the Cr$_2$O$_3$ analysis it is easily shown that the relative volume change $(V_2 - V_1)/V$ is equal to $-\partial K_1/\partial P$, with negative P meaning a compressive applied pressure, which increases the absolute pressure of the solid. Thus the volume change is given by $+\partial K_1/\partial P$, where P is the absolute pressure, and Eq. (15) becomes the Clausius-Clapeyron equation. Using the experimental values given in Sec. II for the two derivatives in Eq. (15) gives $L = 5.05 \times 10^5$ erg/cm^3. Putting the experimental value of $\partial K/\partial T$ given in Sec. II into Eq. (14) gives $L = 7.2 \times 10^5$ erg/cm^3. The difference in the two values for L reflects the discrepancy between the measured and calculated values of $\partial T_M/\partial P_M$ at $P_M = 0$.

At T_M the difference in the Gibbs function G of the two states must be zero.[22] This difference is defined to be

$$G_2 - G_1 = (U_2 - U_1) - T_M(S_2 - S_1) + P_M(V_2 - V_1), \tag{16}$$

where U is the internal energy. The volume change term is numerically negligible so that the latent heat also gives the internal energy difference $U_2 - U_1$ at T_M. At $T = 0$, $U_2 - U_1 = G_2 - G_1$ (again neglecting the volume difference term) and this quantity is $K(T = 0)$, which has the experimental value of 2×10^5 erg/cm^3.

Thus the values obtained above for L imply that the internal energy difference between state 2 and state 1 *increases* between $T = 0$ and T_M, which suggests that the Morin transition can be regarded as occurring because of the entropy difference developed between the two states at $T = T_M$. A better theoret-ical treatment of $a_1(T)$ and $a_2(T)$ might clarify this point.

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[14] Microscopically, it may be that $\partial K / \partial P$ is insensitive to temperature in the range 0–300 K because over this range T is enough less than $T_N = 947$ K that the magnetization is nearly constant. The large variation of K with T in this range probably involves the competition between different large and nearly canceling anisotropy mechanisms which are each slowly varying, but slighlty different functions of T [see the discussion below Eq. (12)].

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