Digital Computer Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts

SUBJECT: **A STATISTICAL MODEL FOR FERROMAGNETISM**

To: David R. Brown

From: Arthur L. Loeb

Date: January 14, 1953

Abstract: Considering exchange and Fermi energy of a system of electrons together with magnetostatic, magnetostrictive and anisotropy forces, the internal energy of a magnetized system can be expressed as a function of its magnetization. As indicated by Slater[1)], the entropy of the system is also a function of magnetization, so that the free energy can be expressed approximately as an even fourth degree polynomial in the magnetization in the absence of an external field. Plotting the free energy vs. magnetization, the curve has either one minimum, or two minima separated by a maximum. The former condition corresponds to para-, the latter to ferromagnetism.

Introduction of an external magnetic field adds a linear term to the free and internal energy functions.

The shift in position of the minima can be calculated, and is used to compute the corresponding net magnetization of the system.

The hysteresis curve can be explained by the existence of the maximum in the internal energy curve, which tends to prevent the system from settling to equilibrium at the lower of the two relative minimum. Increasing the external field eventually causes the higher of the two relative minima to fuse with the maximum into a point of inflection, at which point the entire system will settle in equilibrium around the one remaining minimum. The external field at which this happens is the coercivity.

Other elements of the hysteresis loop are explained similarly.

---

1) Slater: "Quantum Theory of Matter", 1st edition Appendix 22.

## Introduction

The ferromagnetic properties of a system are essentially due to the spins of its electrons. Let us assume first that only two directions of magnetization are to be considered. When the system is unmagnetized, the number of electrons having one direction of spin equals that having the opposite direction of spin. If any electrons are oriented at a finite angle to the directions under consideration, we concern ourselves only with the component of their spin parallel to the directions being considered.

The magnetization mechanism is thought of as the transfer of some electrons from the system with one spin to the system with another spin. This affects both the Fermi energy of the system, and the exchange energy, for either system is generally completely filled up to its top Fermi level, and any additional electrons must go into higher levels (see Figs. 1a and 1b). In Figs. 1a and 1b is plotted the number of electrons per unit energy interval, $\frac{dN}{dE}$, vs. the energy E

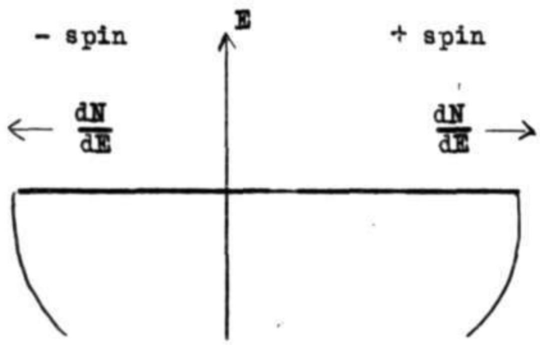


**Fig. 1a**: Unmagnetized system: both the + and the - system are filled to equal levels.

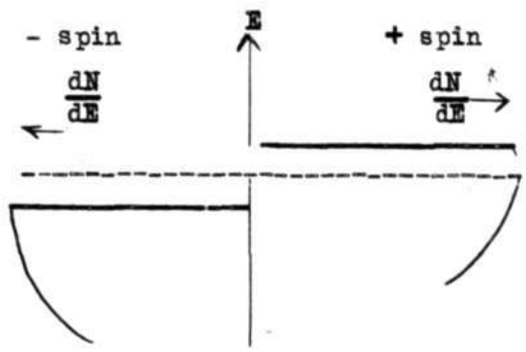


**Fig. 1b**: Magnetized system: excess + spin due to electrons transferred from lower level in negative system to higher one in positive system.

The exchange energy is determined only by the number of pairs of electrons of equal spin; transfer of electrons from one system to the other decreases the number of pairs of the depleted system less than it increases the number of pairs of the other system, so that the transfer increases the total number of pairs of the system. As the exchange energy of two equal spins can be assumed to be negative, and electrons of opposite spin do not have an exchange energy, the total interaction energy decreases with increasing magnetization. For a quantitative discussion of these terms in the magnetization energy, see "Seminar of Magnetization" XVIII, M-1772, Digital Computer Laboratory. As the magnetization M is proportional to the number of electrons transferred, n, we can write:

Change in Fermi energy on magnetization $= \Delta E_F = pM^2$ (equ. 1)

where $p > 0$, a constant inversely proportional to $\frac{dN}{dE}$

Change in exchange energy on magnetization $= \Delta E_e = -qM^2$ (equ. 2)

where $q > 0$, a constant proportional to the exchange energy of two electrons of equal spin.

Anisotropy, magnetostatic and magnetostrictive energies are generally even functions of magnetization, for unless a system is chosen that is biased toward one orientation over the opposite one, the magnitude of the magnetization is the only thing that matters. Thus let us approximate these energies by the expression

$$\Delta E_m = rM^2 + sM^4 \qquad \text{(equ. 3)}$$

where r and s are constants

Then the total energy of magnetization is given by:

$$\Delta E = (p - q + r)\, M^2 + sM^4 \qquad \text{(equ. 4)}$$

This represents the internal energy of magnetization. The entropy of a magnetized system is less than that of an unmagnetized one, because the latter is more random than the former. Slater[1] has expressed the entropy of magnetization by the expression

$$\Delta S = -dM^2 - eM^4, \text{ where } d > 0 \text{ and } e > 0$$

Thus, since the free energy of magnetization $\Delta F = \Delta E - T\Delta S$,

$$\Delta F = (p - q + r + dT)\, M^2 + (s + eT)\, M^4 \qquad \text{(equ. 5)}$$

Both the free and the internal energies are useful quantities. The free energy determines the equilibrium conditions, for thermodynamic equilibrium occurs when the free energy is a minimum. A minimum in the free energy does not occur at the same magnetization as does a minimum in the internal energy, as will be shown by the following argument:

If internal energy were the only term determining the equilibrium magnetization, then its relative minima would correspond to equilibrium magnetizations. However, the entropy of such a system would be quite low, and the tendency for any system to increase its entropy would force the equilibrium back to smaller magnetizations. Thus the minima in the free energy, which actually do determine equilibrium conditions, occur at smaller absolute values of the magnetization than do the minima in the internal energy.

The internal energy is important for considerations of the dynamic behavior of the system. To determine the equilibrium magnetization $M_o$, differentiate equ. 5 with respect to M:

$$0 = \frac{\partial \Delta F}{\partial M} = 2\,(p - q + r + dT)\,M_o + 4\,(S + eT)\,M_o^3 \quad \text{(equ. 6)}$$

Equation 6 has three solutions, one of which is $M_o = 0$. The other two solutions are either real or imaginary:

if $q < P + R + dT$, they are imaginary, and $M_o = 0$ is a minimum.

if $q > p + r + dT$, they are real and minima, while $M_o = 0$ is a maximum.

These two cases are shown in Figures 2a and 2b:

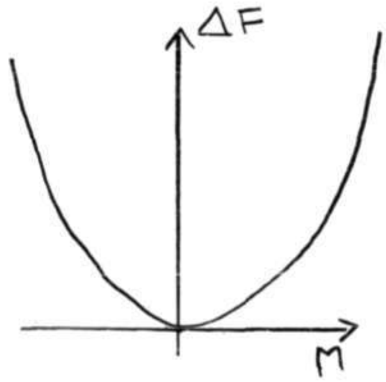


Fig. 2a
$q < p + r + dT$

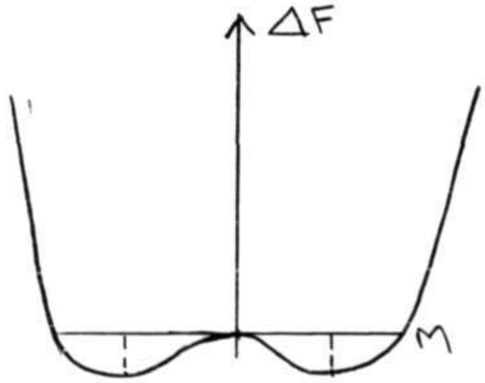


Fig. 2b
$q > p + r + dT$

The minima in Fig. 2 b occur at

$$M_o = \pm \sqrt{\frac{q - p - r - dT}{2\,(s + eT)}} \quad \text{(equ. 7)}$$

Physically we can interpret Figs. 2a and 2b as follows: In Fig. 2a we have a system in which electrons can change their spin easily. Equilibrium is set up between the two systems, with on the average an equal number changing from + spin to - spin as change in the opposite sense. Thus any one electron examined over a finite period of time will eventually have spent an equal time in the negative as in the positive system.

The system of Fig. 2b behaves quite differently, for electrons with spin $-M_o$ have to overcome an internal energy barrier equal to

$$\triangle E = (p - q + r)\, M_o^{\,2} + sM_o^{\,4}$$

in order to reverse its spin. Thus any electron under observation is not at all likely to reverse its spin; the existence of ferromagnetic domains confirms that electrons in ferromagnetic materials do not spontaneously reverse their spin.

It should be noted that the system does not settle into one magnetization, but rather distributes itself around the free energy minima.

Fig. 3 shows the likelihood that a ferromagnetic system has magnetization M

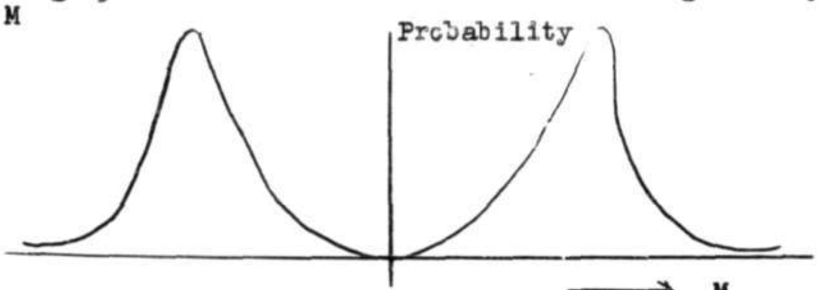


Fig. 3

## Discussion of Magnetic Properties

Equations (3) and (4) express the internal and free energies of a magnetic system in terms of parameters p, q, r, s, d and e. Of these p and q can be calculated from Fermi bands and exchange coupling, r and s from magnetostatic and strictive energies and anisotropies, and d and e from entropy considerations. However, in this report we shall attempt to express several magnetic properties in terms of the free energy curves, and hence obtain parametric relations between these various properties.

The first property is the Curie temperature; this is temperature at which ferromagnetic materials become paramagnetic. Examination of Figs. 2a and 2b shows that these two figures become similar, i.e. the hump in Fig. 2b disappears when

$$q = p + r + dT_c, \text{ where } T_c = \text{the value at which this occurs, namely the Curie point.}$$

Substituting into equ. (4) and (5) this produces:

$$\Delta E = -dT_c M^2 + sM^4 \qquad \text{(equ. 8)}$$

$$\Delta F = d\,(T-T_c)\,M^2 + (s + eT)\,M^4 \qquad \text{(equ. 9)}$$

__Presence of external field__

When an external magnetic field is superimposed on the system, the term $-HM$ must be added to the expressions for $\Delta E$ and $\Delta F$ in equs 8 and 9:

$$\Delta E = -HM - dT_c M^2 + s\,M^4 \qquad \text{(equ. 10)}$$

$$\Delta F = -HM - d(T_c - T)\,M^2 + (s + eT)\,M^4 \qquad \text{(equ. 11)}$$

Figs. 2a and 2b then assume the form shown in Figs. 4a and 4b:

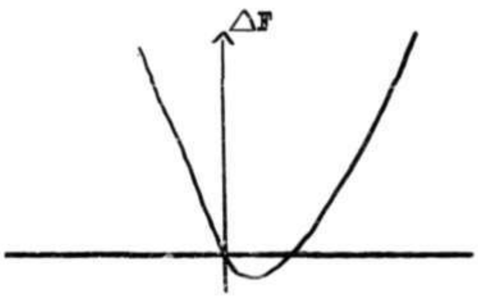


Fig. 4a

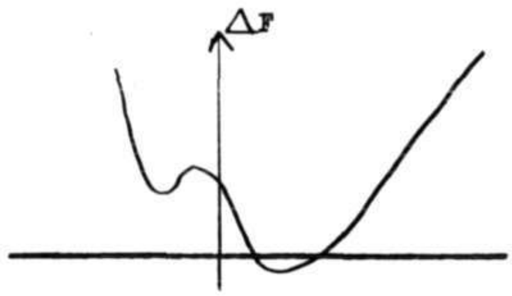


Fig. 4b

Fig. 4a demonstrates that the system now settles easily into equilibrium about a slightly positive magnetization. In Fig. 4b the two relative minima are not now at equal heights, so that equilibrium would favor the one with positive magnetization. However, in order to reach equilibrium, many negative spins must be reversed, and hence must overcome the energy barrier, which may still be considerable even though it does decrease in magnitude with increasing field. Only when the external magnetic field reaches a value $H_c$ (coercivity) at which the hump vanishes can the system reach equilibrium. Actually there is always a finite speed with which the system goes over an even finite hump, as given by equ.(12):

$$v \propto e^{-\frac{\Delta E_h}{kT}} \qquad \text{(equ. 12)}$$

where v is the velocity, $\Delta E_h$ the energy of the hump.

Thus it is seen that in the situation described in Fig. 4b, there is a finite velocity from left to right as well as from right to left, but because $\Delta E_h$ for the former is much smaller than that for the latter, the net effect favors the positive magnetization. If a ferromagnetic system is subjected for a long time to a field H less than its coercivity $H_c$ we would expect its magnetization to increase very slowly, because it will gradually pass from the metastable state corresponding to some of the electrons still at the higher rel. min. to the stable state corresponding to all electrons at the lower rel. min.

The hysteresis loop: qualitative evaluation

Fig. 5 shows a hysteresis loop with virgin curve; in this section we will correlate Figs. 5 and 4b.

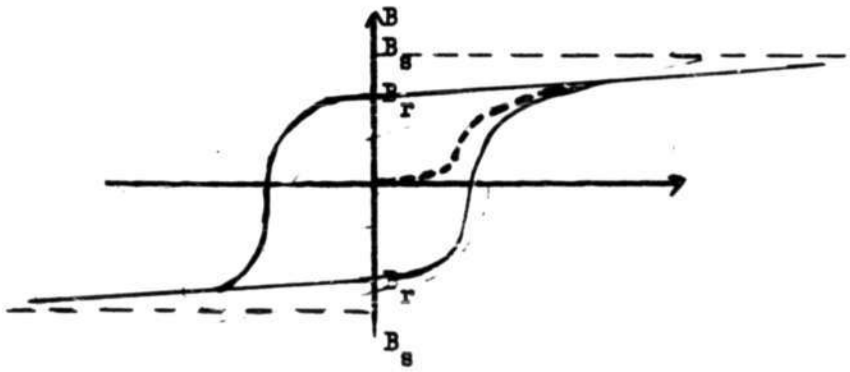


Fig. 5

Starting at the origin we have the situation described by Fig. 2b the magnetization is equal in both directions. When a field H is imposed on the system, Fig. 4b describes the energy; the only increase in magnetization is due to the fact that the curve now becomes more asymmetrical about the relative minima, so that the distribution around each of the relative minima tends toward the side of higher (more positive, less negative) magnetization. However, half of the electrons are still captured in the higher rel. min. by the energy hump in between the two minimum. When the field increases, the velocity of the systems travelling over the hump increases very rapidly (exponentially) until the hump disappears because the higher rel. min. and the max. fuse to form a point of inflection. Then the magnetization becomes very large, because all electrons settle about one minimum, at high magnetization. Increasing the field now has a similar effect as it does on paramagnetic substances for it will shift the minimum somewhat to the right. Also, it will distort the curve some more favoring higher magnetization so that the probability of finding the system in a magnetization less than that corresponding to the minimum in the energy curve is less than finding it in a magnetization above that of the energy minimum. Both influences will increase the average magnetization somewhat, though it will tend to the asymptote corresponding to $B_s$.

When the field is reversed, the situation will reverse itself until $H = H_c$. Then, however, the electrons will not spontaneously go into the higher rel. min. which is again created as soon as $H < H_c$. On the contrary, even when $H = 0$ and $\Delta F$ is again described by Fig. 2b, all electrons are captured in the righthand minimum, and the consequent distribution leads to the remanence $B_r$. When the field H becomes negative, the system will pick up speed in going over the hump, for now the righthand relative minimum is higher than the left hand one. The magnitude of the hump therefore determines the squareness of the hysteresis loop, for we are now on the "demagnetization" portion of the loop. As before, the hump disappears when $H = -H_c$, and from here on the procedure is completely symmetrical with what has preceded.

The magnitude of the hump is therefore seen to determine at least:

a) Curie temperature

b) Coercivity

c) Squareness Ratio

<u>Coercivity</u> <u>and</u> <u>Curie</u> <u>temperature</u>

Since the minima in the <u>free</u> energy curves occur at smaller absolute values of the magnetization than do those in the <u>internal</u> energy, (see p.3), the fusion of a rel. min. with the maximum occurs for the <u>free</u> <u>energy</u> at a somewhat lower value of H than it does for the <u>internal</u> energy, so that calculation of the critical value of H for the F curve should give at least a lower limit to the coercivity.

Differentiating equ. 11, we get extrema for:

$$0 = \frac{\partial \Delta F}{\partial M} = - H - 2d\,(T_c - T)\, M + 4\,(S + eT)\, M^3 \qquad \text{(equ. 13)}$$

Since equ. 13 has a double root (labeled $M = M_a$) and a single root (labeled $M = M_c$), it should be in the form:

$$(M - M_a)^2 \, (M - M_c) = 0$$

This can be expanded in the form:

$$M^3 - (2M_a + M_c)\, M^2 + (M_a + 2M_c)\, M_a\, M - M_a^2\, M_c = 0 \quad \text{(equ. 14)}$$

Comparing (equ. 13) and (equ. 14) and equating coefficients of equal powers in M, we find:

$$M_c = -2\, M_a \qquad \text{(equ. 15)}$$

This confirms the fact that $M_c$ and $M_a$ are on opposite sides of the line $M = 0$, as implied in the drawings.

$$(M_a + 2M_c)\,M_a = -\frac{d\,(T_c - T)}{2\,(s + eT)}$$

$$M_a^2\,M_c = \frac{H}{4\,(s + eT)}$$

These equations lead to the expression:

$$M_c = \sqrt{\frac{2d(T_c - T)}{3\,(s + eT)}} \qquad \text{(equ. 16)}$$

where $M_c$ is the most likely value when $H = H_c$, which is not necessarily the average value, because the energy curves are not symmetrical about $M = M_c$

Another relation to be derived from these relations is:

$$M_c = \frac{3\,H_c}{2d(T_c - T)} \qquad \text{(equ. 17)}$$

thus relating most likely magnetization when $H = H_c$ to the coercivity and Curie temperature with only one entropy parameter involved.

Eliminating $M_c$ between equs. (16) and (17) gives:

$$H_c = \frac{1}{3}\,\frac{\left[2d\,(T_c - T)\right]^{\frac{3}{2}}}{\left[3\,(s + eT)\right]^{\frac{1}{2}}} \qquad \text{(equ. 18)}$$

As expected $H_c = 0$ at the curie point.

Conclusions:

With the aid of the model just described, the hysteresis loop has been traced qualitatively. A few critical points of the loop have been found quantitatavely as function of temperature in terms of parameters d and e (entropy parameters) and s (magnetic and anisotropy parameters).

On the basis of the energy curves the average value of M can be found for any H, which corresponds to calculating the hysteresis loop.

Without actually computing s, e and d, equs. 17 and 18 could be checked simply by plotting various observed values against each other to see if these simple laws hold. This would actually be a more valuable check than computing on the basis of s, e and d, because the numerical values of these parameters depend on assumptions and knowledge about the exact microstructure of the system, and hence would be expected to be correct only to orders of magnitude. The general behaviour of the elements of the hysteresis loop, on the other hand, would not be as sensitive to the exact value of the parameters.

Corrollary: Many directions of magnetization.

We have considered here only + or - magnetizations, assuming one preferred direction. This is of great interest to us, because those materials that are satisfactory for us are at least cast into such a shape that only two senses of magnetization are likely.

For two dimensional systems of magnetization Figs. 2b and 4b would become a hill with a moat around it. In Fig. 4b this moat would rise on one side, descend on the other side of the hill. In Fig. 2b the moat would be equally deep in isotropic material, but would contain holes and "passes" in case of certain directions of easy magnetization. The "passes" would be saddle points, the holes relative minima, the hill a maximum in the surface F vs. M. It is seen that now it would be easier for the system to go around the hill rather than over it, and in our one-dimensional system we should have realized this when discussing the difficulty of going over the top. Going around the top of the hill would mean gradually changing the direction of magnetization through $180^{\circ}$, i.o.w. rotation. Correction for rotation would tend to make the hysteresis loop somewhat more "round shouldered" than as calculated by the one-dimensional model.

Imposing a field would alter the relative positions of passes, hills, and the hilltop, and these relative positions would determine the relative probabilities of rotation (around the hill) and domainwall motion (over the hill). The justification of considering domainwall motion as a motion "over the hill" is that for walls between antiparallel domains wall motion requires quick reversal of individual spins. Since the walls have finite width, this reversal is not quite abrupt; therefore the system travels just around the very top of the hill. The wider the domain wall, the less the exchange energy in the wall, and the lower the system will cut off in going around the top rather than over it.

Signed Arthur L. Loeb
(Arthur L. Loeb)

ALL;jrt

Approved DRB
(David R. Brown)

cc: Groups 62 and 63
Prof. von Hippel
Prof. L. Harris