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THERMODYNAMICS OF THE HEISENBERG FERROMAGNET IN AN APPLIED MAGNETIC FIELD

by Lawrence Flax
Lewis Research Center
Cleveland, Ohio

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by Lawrence Flax

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

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ABSTRACT

The anisotropic Heisenberg ferromagnet formalism developed previously is examined to include an applied magnetic field for the isotropic case in the random phase approximation. Thermodynamic quantities such as magnetization, susceptibility and the derivative of magnetization with respect to temperature are studied near the Curie point.

INTRODUCTION

According to the Weiss theory a ferromagnetic material possesses an internal field which is proportional to the magnetization. As the temperature of a ferromagnet is increased, the magnetization decreases until, at a temperature known as the Curie temperature T_c, the material becomes paramagnetic. The process by which this change from ferromagnetism to paramagnetism occurs is referred to as the ferromagnetic phase transition. Investigations have shown that electrical, mechanical, and many thermodynamic properties of a material are altered when the material undergoes a phase transition.

The effect of an external magnetic field is twofold: (1) the magnetization is increased above its zero field value and (2) the critical point disappears. Even though increasing temperature tends to destroy spin alinement, the field causes some ordering to be present. Thus instead of an abrupt change at the critical temperature there is a more gradual transition.

This report is concerned with the investigation of the thermodynamic properties of the Heisenberg ferromagnet in an external magnetic field. The quantities studies are the magnetization, susceptibility and the derivative of magnetization with respect to temperature. The last of these can be used to calculate entropy and the magnetocaloric effect, which are useful for investigating various recently proposed magnetic refrigeration systems.[1-2]

Model

The Heisenberg model is based on a solid where the magnetic electrons are in states localized about the lattice sites with an exchange interaction taking place between electron pairs. The model does not take into account itinerant electrons and is considered valid for insulating ferromagnets such as EuO but not for conductors such as iron and nickel. However, it appears that this model gives better results for conductors at low temperatures than those calculated from a band theory approach as shown by Argyle, Charap and Pugh.[3] It should be noted, however, that the Heisenberg model with its surprising success does not take into account the spreading of the electronic energy levels into bands.

The Heisenberg ferromagnet with spin 1/2 was analyzed by Bogolyubov and Tyablikov[4] using the techniques of double-time, temperature dependent Green's functions. An excellent review of Green's functions and Tyablikov's application of them to ferromagnetism is given by D. N. Zubarev[5] and references contained therein.

The Hamiltonian for the Heisenberg model is

$$H = -g\mu_B H_o \sum_i S_i^z - \sum_{i,} J_{ij}\left[S_i^z S_j^z + \frac{1}{2}\left(S_i^+ S_j^- + S_i^- S_j^+\right)\right] \tag{1}$$

where

$$S_j^{\pm} = S_j^x \pm iS_j^y \tag{2}$$

μ_B is the Bohr magneton, g is the Lande' g factor, H_o is the applied magnetic field which is assumed to be along the z-direction, S_i is the spin operator for a spin at site i, and J_{ij} is the exchange interaction between spins on sites i and j. The sum is carried over all sites in the crystal. The exchange interaction is assumed to be a function only of the distance between sites. The self-exchange terms such as J_{ii} or J_{jj} are zero.

Calculation of Thermodynamic Quantities

Since the thermodynamic quantities of interest are the magnetization and entropy of the system, one is interested in correlation functions of the form $\langle S_g^- S_m^+ \rangle$ and hence of the Green's function $\langle\langle S_g^+; S_m^- \rangle\rangle$

Starting with the Green's function $\langle\langle S_g^+; S_m^- \rangle\rangle$ one can derive the correlation function in the random phase approximation. The results are:

$$\langle S_m^- S_g^+ \rangle = \left(\frac{1}{N}\right) \sum_K 2 \langle S_g^z \rangle e^{ik\cdot(g-m)} \left(e^{\beta E_k} - 1 \right)^{-1} \tag{3}$$

where

$$E_k = 2 \langle S^z \rangle J(0) \left[1 - \frac{J(k)}{J(0)} \right] + \mu_B g H_o \tag{4}$$

and

$$J(k) = \sum_m J_{gm} e^{ik\cdot(g-m)} \tag{5}$$

The sum in equation (3) is over all N lattice vectors in the first Brillouin zone.

The applied magnetic field is assumed sufficient to orient the net magnetization along the direction of the field. The field also induces

additional long-range order. The long-range order is thus due to the internal field and to the applied magnetic field. The thermal average of the z component of the spin, $\langle S^z \rangle$, is defined as the magnetization per site and is a measure of this long-range order.

The magnetization, S^z is calculated from the relation

$$\langle S^z \rangle = \frac{1}{2[1 + 2\varphi]} \tag{6}$$

where

$$\varphi = \left(\frac{1}{N}\right)\sum\left(e^{\beta E_k} - 1\right)^{-1} = \left(\frac{1}{2N}\right)\sum_k \left[\coth\frac{(\beta E_k)}{2} - 1\right] \tag{7}$$

The sum in equation (7) must be evaluated over all values of k in the first Brillouin zone of the appropriate lattice. Except at the very low- and high-temperature limits, numerical methods are usually used. Such numerical solutions are, however, somewhat difficult. One of the purpose of this paper is to show that analytical solutions of equation (7) are possible.

For crystals with cubic symmetry, such as bcc, one can replace the sum which appears in equation (7) by an integral. Using the same techniques developed by Flax and Raich[6-8] one can obtain the magnetization:

$$\langle S^z \rangle = \frac{1}{2\Delta} \tag{8}$$

where

$$\Delta = \left(\frac{1}{P}\right)\left[\frac{2K(k)}{\pi}\right]^2 + \coth P - \frac{1}{P} + \left(\frac{Q^2}{8}\right)\left[\operatorname{csch}^2 P \coth P - \frac{1}{P^3}\right] \tag{9}$$

$$P = \frac{\alpha}{2 + Q}$$

$$\alpha = \frac{\mu_B g H_o}{[J(0)\tau]} = \frac{H'}{\tau} \tag{11}$$

$$\tau = \frac{k_B T}{J(0)} \tag{12}$$

$$Q = \frac{\langle S^z \rangle}{\tau} \tag{13}$$

and K(k) is a complete elliptic integral of first kind with

$$k^2 = \left(\frac{1}{2}\right)\left[1 - \sqrt{1 - \left(\frac{Q}{P}\right)^2}\right] \tag{14}$$

Equations (8) and (9) give $\langle S^z \rangle$ a function of temperature, magnetic field and magnetization.

Figure 1 shows a plot of $\langle S^z \rangle$ as a function of temperature for several values of H' for a bcc lattice. When H' equals zero there are no solutions for $\langle S^z \rangle$ above a critical temperature T_c, that is, the Curie temperature. This is the point where long range order disappears and above which the spins are completely disordered. For non-zero H' the ferromagnetic transition occurs over a range of temperatures which forms a Curie region, so that the transition is smeared out and results in the appearance of a "tail."

The cause of the "tail" is that the long-range order persists through the effect of the applied magnetic field. The higher the field, the greater is the broadening of the transition.

Figure 2 shows a plot of $\langle S^z \rangle$ as a function of H' for several values of τ for a bcc lattice. As is seen from the figure the magnetization has a nonlinear dependence on the magnetic field near the Curie point ($\tau = 0.3588$). This nonlinearity in the transition region can be attributed to the exchange interaction. This behavior persists as the temperature is increased for small magnetic field strengths. For high field and

high temperature the magnetization curve becomes linear. This has been experimentally verified for many ferromagnetic substances.[10]

MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility χ is defined as

$$\chi = \frac{\langle S^z \rangle}{H'} = \frac{Q}{\alpha} \tag{15}$$

Using equations (8) through (14) together with equation (15) one obtains

$$\chi = \frac{1}{2\alpha\tau\,\Delta'} \tag{16}$$

where

$$\Delta' = \left(\frac{1}{P}\right)\left[\frac{2K(k_1)}{\pi}\right]^2 + \coth P - \frac{1}{P} + \alpha^2\,\frac{\chi^2}{8}\left[\operatorname{csch}^2 P \coth P - \frac{1}{P^3}\right] \tag{17}$$

$$P = \frac{\alpha}{2} + \frac{(1 + 2\chi)}{2} \tag{18}$$

and

$$k^2 = \frac{1}{2}\left(1 - \sqrt{1 - \left(\frac{2\chi}{1 + 2\chi}\right)^2}\right) \tag{19}$$

For a given ferromagnetic material the spontaneous magnetization can occur only below a critical temperature T_c. Well above the Curie temperature, such materials are found experimentally to behave paramagnetically, and have a susceptibility which follows the Curie - Weiss law, namely

$$\chi = \frac{C}{(T - \theta)} \tag{20}$$

in which C is the Curie constant and θ is called the paramagnetic Curie temperature. θ is usually somewhat higher than T_c.

A plot of $1/\chi$ as a function of τ from equation (16), is shown in figure 3. As required the curve becomes linear at temperature sufficiently far above the Curie point. The nonlinearity in the neighborhood of the Curie point agrees qualitatively with experiment.[11] Below the Curie temperature, T_c, ferromagnetic materials show a marked increase in susceptibility.

CALCULATION OF THERMODYNAMIC QUANTITIES

For an adiabatic process, where there is no change in entropy

$$d\tau = -\frac{\tau}{C_{H'}}\left(\frac{\partial S^z}{\partial \tau}\right)_{H'} dH' \tag{21}$$

where $C_{H'}$ is the magnetic specific heat. Since $(\partial S^z/\partial\tau)_{H'}$ is negative for a ferromagnet, an increase in field produces an increase in temperature; moreover, the increase is expected to be largest near the critical point. This is known as the magnetocaloric effect.

The entropy, which is a measure of the order of the system, can be calculated from

$$S = \int_0^{\tau} \frac{C_{H'}}{\tau}\, d\tau + \int_0^{H'} \left(\frac{\partial \langle S^z \rangle}{\partial \tau}\right)_{H'} dH' \tag{22}$$

The change of magnetization with respect to the reduced temperature at constant applied field can be derived from equations (8) and (9) as follows:

$$\left(\frac{d\langle S^z\rangle}{d\tau}\right)_{H'} = -\frac{1}{2}\left(\frac{1}{\Delta^2}\right)\left[\left(\frac{\partial \Delta}{\partial \langle S^z\rangle_{\tau}}\right)\frac{d\langle S^z\rangle}{d\tau} + \left(\frac{\partial \Delta}{\partial \tau}\right)_{\langle S^z\rangle}\right] \tag{23}$$

$$\left(\frac{\partial S^z}{\partial \tau}\right)_{H'} = - \frac{\left(\frac{\partial \Delta}{\partial \tau}\right)_{\langle S^z \rangle}}{\left[2\Delta^2 + \left(\frac{\partial \Delta}{\partial \langle S^z \rangle_\tau}\right)\right]} \tag{24}$$

where

$$\left(\frac{\partial \Delta}{\partial \langle S^z \rangle}\right) = - \frac{1}{p^2 \tau}\left[\frac{2K(k)}{\pi}\right]^2$$

$$+ \frac{2K(k)}{\pi^2 p^2 k}\left\{\left[\frac{E(k) - k'^2 K(k)}{kk'^2}\right]\left[\frac{\sqrt{\left(\frac{\alpha^2}{4}\right) + \alpha Q}}{p\tau}\right.\right.$$

$$\left.\left. - \frac{\alpha}{2\sqrt{\frac{\alpha^2}{4} + \alpha Q}}\right]\right\}\frac{-\operatorname{csch}^2 p}{\tau} + \frac{1}{p^2 \tau}$$

$$+ \frac{Q}{4\tau}\left[\operatorname{csch}^2 P \coth^2 P - \left(\frac{1}{P}\right)^3\right]$$

$$- \frac{Q^2}{4\tau}\left[\operatorname{csch}^2 P \coth^2 p - \frac{3}{2P^4} + \frac{1}{2}\operatorname{csch}^4 p\right] \tag{25}$$

$$\left(\frac{\partial \Delta}{\partial \tau}\right)_{\langle S^z \rangle} = \frac{1}{P\tau}\left[\frac{2K(k)}{\pi}\right]^2 + \left(\frac{P}{\tau}\right)\operatorname{csch} P - \frac{1}{P\tau} - \frac{Q^2}{8\tau}\left[2 \operatorname{csch}^2 P \coth P\right.$$

$$\left. + \left(\frac{2}{P}\right)^3 - 2P \operatorname{csch}^2 P \coth P^2 - \operatorname{csch}^4 P\right] \tag{26}$$

$$k' = \sqrt{1 - k^2} \tag{27}$$

and

E(k) is a complete elliptic integral of the second kind (28)

Figure 4 shows a plot of $(\partial \langle S^z \rangle / \partial \tau)_{H'}$ as a function of temperature for several values of H' for a bcc lattice. These derivatives have not previously been obtained analytically.

CONCLUSIONS

The thermodynamic properties of the Heisenberg ferromagnet in a magnetic field have been investigated theoretically by using a random phase approximation. Expressions are derived from which the thermodynamic parameters can be calculated. The derivative of the magnetization with reduced temperature is obtained for use in the calculation of the magnetocaloric effect and entropy. The analysis predicts that:

1. In the presence of a magnetic field the ferromagnetic transition is smeared out. This results in the appearance of a tail in the magnetization versus temperature curve. Increasing the magnetic field increases the broadening of the transition.

2. There is a nonlinear dependence of the magnetization upon field at the Curie point. When the temperature is raised, the nonlinearity remains in the weak field region, but in the strong field region the magnetization becomes linear with field.

3. Well above the Curie point the susceptibility follows the Curie - Weiss law (χ^{-1} proportional to temperature). In the immediate neighborhood of the Curie point, however the dependence of -1 on temperature is nonlinear. These results are in qualitative agreement with experiment.

REFERENCES

1. J. R. Van Geuns, University of Leiden Thesis (1966).
2. G. V. Brown, XIII International Congress of Refrigeration (1971).
3. B. E. Argyle, S. H. Sharap, and E. W. Pugh, Phys. Rev. 132, 205 (1963).
4. N. N. Bogolyubov, and S. V. Tyablikov, Soviet Phys. - Doklady 4, 589 (1959).
5. D. N. Zubarev, Soviet Phys. - Uspekhi 3, 320 (1960).
6. L. Flax and J. C. Raich, Phys. Rev. 185, 797 (1969).
7. L. Flax and J. C. Raich, NASA TN D-5286 (1969).
8. L. Flax and J. C. Raich, Phys. Rev. B2, 1338 (1970).
9. L. Flax, NASA TN D-6037 (1970).
10. K. P. Belov, Magnetic Transitions (Consultants Bureau, New York, 1959).
11. P. Weiss and R. Forrer, Ann. Phys. 5, 153 (1926).

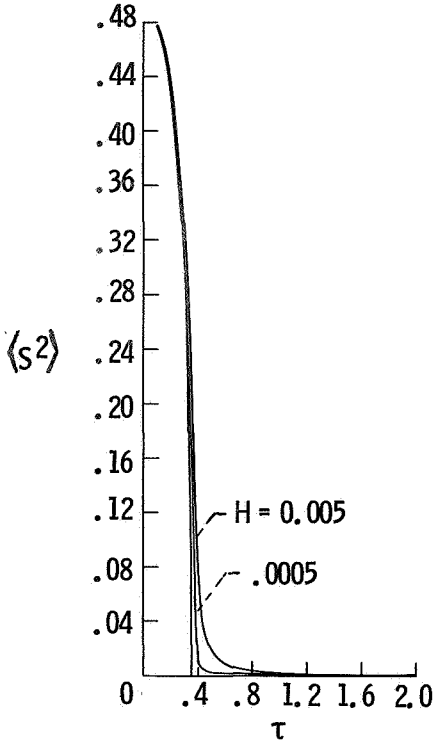

Figure 1. - Magnetization as a function of temperature.

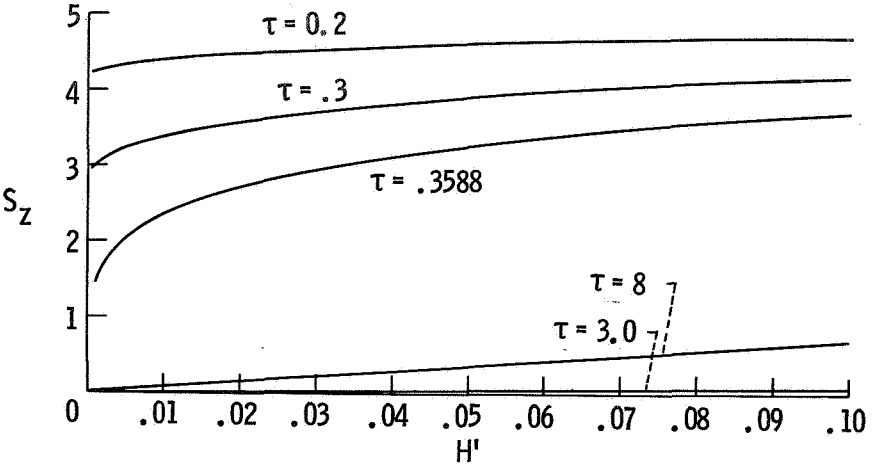

Figure 2. - Magnetization as a function of reduced magnetic field.

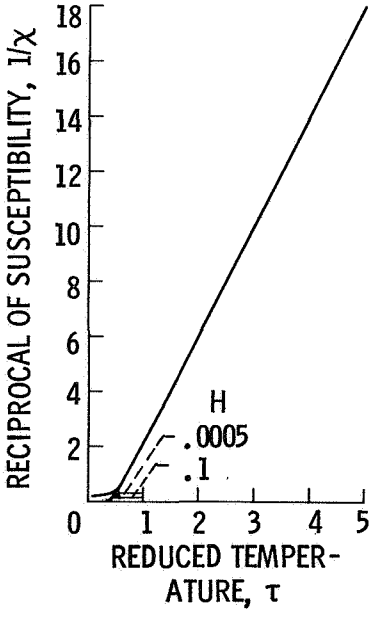

Figure 3. - Reciprocal of susceptibility as a function of reduced temperature.

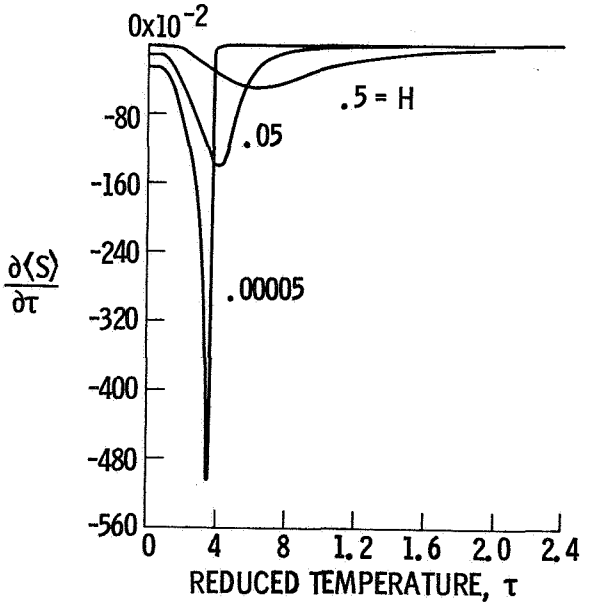

Figure 4. - Partial derivative of magnetization with respect to reduced temperature for constant reduced magnetic field as a function of reduced temperature.