PHYSICAL REVIEW VOLUME 138, NUMBER 1A 5 APRIL 1965

Spatial Variation of the Magnetization Across a Ferromagnetic Thin Film in the Bethe-Peierls-Weiss Approximation*

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(Received 9 November 1964)

The variation of the magnetization across a ferromagnetic film as a function of temperature and film thickness has been calculated in the Bethe-Peierls-Weiss approximation. In this approximation the Heisenberg exchange interaction between a given spin and the shell consisting of its nearest neighbors is treated exactly. The interaction of this shell with the rest of the sample is treated approximately, as an interaction with a molecular field. The extension to thin films was made by allowing this molecular field to vary across the film in the manner used by Valenta for the molecular-field approximation. The finite thickness of the film had little effect on the temperature variation of the magnetization, reducing the Curie temperature by only a few percent from the bulk value even for films as thin as eight layers. The spatial falloff of the magnetization at the surface was even more abrupt than in the molecular-field case and almost independent of film thickness. For a film of twenty layers, the magnetization fell at the surface to 60% of its value at the center and almost the entire drop occurred within four layers. The temperature dependence was found to be very sensitive to the method of determining the molecular field.

INTRODUCTION

In a ferromagnetic thin film the spontaneous magnetization varies in space across the thickness of the film because the magnetic moments near the surfaces see a different environment from that seen by those nearer the center. In particular, for the idealized case considered here, that of a Heisenberg exchange Hamiltonian restricted to nearest-neighbor interactions, a spin located in the surface plane of a simple cubic array has only five nearest neighbors as contrasted with the six surrounding an interior spin. The surface spin thus experiences a smaller exchange force, is less completely aligned with the over-all moment of the film, and consequently exerts a somewhat smaller exchange force on its neighbors than would a spin nearer the center. Thus, the effect is propagated into the interior of the film. It is of interest to know how great this decrease in magnetization at the surface is, how far it extends into the film, and what effect it has on the temperature dependence of the magnetization and on the Curie temperature.

The greatest effects occur at temperatures near the Curie temperature, and the spatial variation diminishes as all the planes of the film approach saturation with decreasing temperature. A high-temperature treatment is thus required. Methods are well known for treating the temperature variation in the bulk case. The thin film represents a good starting point for the treatment of spatial variations since it is, in a sense, a one-dimensional problem, with all the quantities of interest depending only on the spatial coordinate perpendicular to the film surfaces. Valenta[1] approached the problem by computing the Curie temperature of a film in an approximation equivalent to the molecular-field (MF) approximation for the bulk case. While the latter approximation gives a qualitatively correct explanation for the temperature dependence of the bulk magnetization, it predicts a Curie temperature which is too high by 60%. The next higher approximation, the Bethe-Peierls-Weiss (BPW) approximation essentially eliminates this error and therefore represents an important correction. The present paper describes the extension of the BPW method to the spatially varying case and presents results for the temperature and spatial variation of the magnetization both for this new model and for that considered by Valenta. Section I compares the assumptions of the four approximations just mentioned. Section II discusses the methods for solving the equations arising in the approximation of this paper. Section III presents the results.

I. COMPARISON OF APPROXIMATIONS

In each of the approximations to be discussed, the quantity of interest is the thermal average value of the projection of the spin along the direction of the total magnetization (some external field is assumed to fix this direction, but that external field can be allowed to go to zero in the calculations without affecting the result). These thermal averages are calculated in each case by taking the trace of the spin projection in question times the density matrix for a Gibbs ensemble.

In the MF approximation for the bulk case, one assumes that the interaction of one spin with the others can be replaced by the interaction of that spin with an effective molecular field given by the average value of the component of the nieghboring spins in the direction of the over-all magnetization. Valenta in extending this idea to the thin film allowed the molecular field to vary across the thickness of the film, defining it for any plane of spins in terms only of the neighboring spins in that plane. The spatial variation then arises because the field outside the surface is zero.

Weiss[2] viewed the molecular-field approximation as the first in a series of successively higher approximations in which the interactions of the spins within successively

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* Supported by the Lockheed Independent Research Fund.

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larger spheres surrounding a given site are treated exactly, while the effect of the spins outside these spheres is approximated by a molecular field. Thus in the MF approximation the sphere contains only the central atom. In the Bethe-Peierls-Weiss approximations it contains the central atom together with its nearest neighbors. Weiss estimates that the higher approximations can be expected to give a negligible correction. The value of the molecular field in the BPW approximation is determined by the requirement that the same average value of the spin component along the magnetization be obtained for the central atom as for one of its nearest neighbors.

The approximation of the present paper is the extension to the film of the BPW approximation. A different molecular field is defined for each plane of the film. A separate calculation is performed with the central atom situated in each plane. Each neighbor atom interacts with the central atom and with the molecular field appropriate to its own plane. The molecular fields are adjusted so that the average spin projection of the central atom and of one of its nearest neighbors in the same plane are equal for each plane. A summary of the mathematical features of the four approximations can be given as follows:

MF:

$$\bar{S}^z=\mathrm{Tr}(S^z e^{-H/kT}) \tag{1}$$

$$H=-S^z h, \tag{2}$$

$$h=2J(6\bar{S}^z). \tag{3}$$

Valenta:

$$\bar{S}^z{}_i=\mathrm{Tr}(S^z{}_i e^{-H_i/kT}) \tag{4}$$

$$H_i=-{}_iS^z h_i, \tag{5}$$

$$h_i=2J(\bar{S}^z{}_{i-1}+4\bar{S}^z{}_i+\bar{S}^z{}_{i+1}). \tag{6}$$

BPW:

$$\bar{S}_z=\mathrm{Tr}(S^z e^{-H/kt}), \tag{7}$$

$$H=-2J\mathbf{S}\cdot\sum_{j=1}^{6}\mathbf{S}_j-h\sum_{j=1}^{6}S_j{}^z, \tag{8}$$

h chosen so that

$$\mathrm{Tr}(S^z{}_j(e^{-H/kT})=\mathrm{Tr}(S^z e^{-H/kT}). \tag{9}$$

Present:

$$\bar{S}_{zi}=\mathrm{Tr}(S_i{}^z e^{-H_i/kT}), \tag{10}$$

$$\begin{aligned}H_i=&-2J\mathbf{S}_{i,0}\cdot(\mathbf{S}_{i-1}+\sum_{j=1}^{4}\mathbf{S}_{i,j}+\mathbf{S}_{i+1})\\&-h_{i-1}S^z{}_{i-1}-h_i\sum_{j=1}^{4}S^z{}_{i,j}-h_{i+1}S^z{}_{i+1},\end{aligned} \tag{11}$$

h_i chosen so that

$$\mathrm{Tr}(S^z{}_{i,1}e^{-H_i/kT})=\mathrm{Tr}(S^z{}_{i,0}e^{-H_i/kT}). \tag{12}$$

In each case, H is the Hamiltonian, h is a molecular field, subscripts i refer to planes of the film, and subscripts j refer to nearest neighbors of the central spin. In Valenta's approximation, the surface condition is imposed by making $h_{i-1}=0$ for i at the surface. In the present approximation all terms in $i-1$ are eliminated from the Hamiltonian at the surface.

II. METHOD OF SOLUTION

The dimensionality of the Hamiltonian is equal to the number of states which can be formed from the spin functions for the seven spins $\mathbf{S}_{i-1}$, $\mathbf{S}_{i0}$, $\mathbf{S}_{i1}$, $\mathbf{S}_{i2}$, $\mathbf{S}_{i3}$, $\mathbf{S}_{i4}$, $\mathbf{S}_{i+1}$ and is thus 2^7 or 128. The 128×128 Hamiltonian matrix can, however, be reduced with respect to the constants of the motion, T and S_z, where

$$T=\left|\sum_{j=1}^{4}\mathbf{S}_{ij}\right| \quad\text{and}\quad S_z=S^z{}_{i-1}+\sum_{j=0}^{4}S^z{}_{ij}+S^z{}_{i+1}. \tag{13}$$

The j subscript again denotes the various spins in plane i. After this reduction the Hamiltonian consists of two 8×8 blocks (for $T=2$, $S_z=\frac{1}{2}$ and $-\frac{1}{2}$, eight 7×7's, eight 4×4's, four 3×3's, and twelve 1×1's). A typical one of these blocks, that for $T=2$, $S_z=\frac{5}{2}$, is given below with rows and columns labeled by values of T^z, $S^z{}_{i-1}$, $S^z{}_{i+1}$, $S^z{}_{i0}$ in that order:

$$\begin{array}{cccc}
\begin{matrix}2,+\frac{1}{2},\\+\frac{1}{2},-\frac{1}{2}\end{matrix} & \begin{matrix}2,+\frac{1}{2},\\-\frac{1}{2},+\frac{1}{2}\end{matrix} & \begin{matrix}2,-\frac{1}{2},\\+\frac{1}{2},+\frac{1}{2}\end{matrix} & \begin{matrix}1,+\frac{1}{2},\\+\frac{1}{2},+\frac{1}{2}.\end{matrix}\\
\begin{matrix}2h_i+\frac{1}{2}h_{i+1}\\+\frac{1}{2}h_{i-1}+3J\end{matrix} & J & J & -2J\\
J & \begin{matrix}2h_i+\frac{1}{2}h_{i+1}\\-\frac{1}{2}h_{i-1}-2J\end{matrix} & 0 & 0\\
J & 0 & \begin{matrix}2h_i-\frac{1}{2}h_{i+1}\\+\frac{1}{2}h_{i-1}-2J\end{matrix} & 0\\
-2J & 0 & 0 & \begin{matrix}h_i+\frac{1}{2}h_{i+1}\\+\frac{1}{2}h_{i-1}-2J\end{matrix}
\end{array}$$

In this representation, it will be noted that the matrix for $S^z{}_{i0}$ is diagonal. It will be written as $(S^z{}_{i0})_{lm}=M_l\delta_{lm}$. For given values of the ratios h/J, the above blocks can be diagonalized and their eigenvalues and eigenvectors obtained. If the eigenvalues and the unitary eigenvector matrix thus computed are denoted by E_l and A_{lm}, respectively, the quantity $\bar{S}^z{}_{i0}$ is easily obtained as follows:

$$\begin{aligned}\bar{S}^z{}_{i0}&=\mathrm{Tr}(S^z{}_{i0}e^{-H_i/kT})\\&=\textstyle\sum_l\langle l|S^z{}_{i0}|l\rangle e^{-JE_l/kT}\\&=\textstyle\sum_l A^2{}_{ml}M_m e^{-JE_l/kT}.\end{aligned} \tag{14}$$

While $S^z{}_{i1}$ is not diagonal in either the true-energy eigenfunction representation or in the representation used above, it can be seen that it does not connect states within a given block, but only states of different T. Consequently, $S^z{}_{i1}$ is given by an expression of the same

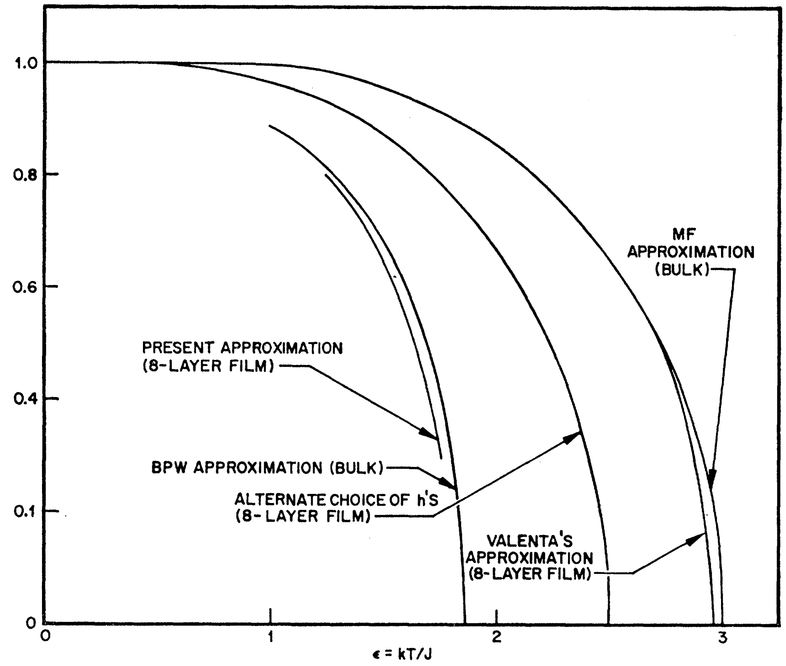

FIG. 1. Temperature dependence of the magnetization in the various approximations.

form as (14) above. The quantities which correspond to the M_m's in that equation can be calculated in an elementary manner using the coefficients for addition of angular momentum. They will not all be integer multiplies of $\frac{1}{2}$ as were the M_m's. The details of the calculation are modified slightly at the surface of the film, since the Hamiltonian there is different, but the principle of the calculation is exactly the same.

Thus, a method has been outlined for calculating, given h_{i-1}, h_i, h_{i+1} and $\epsilon = kT/J$, the corresponding $S^z{}_{i0}$ and $S^z{}_{i1}$, and it remains only to find a consistent set of h_i, $i=1$, N, which satisfy the criterion (12). This is accomplished by a two-stage iterative process. The outer iterations proceed across the film thickness, computing at each point i a value of h_i satisfying (12) for values of h_{i-1} and h_{i+1} already computed. The process is begun by guessing initial values for the h_i's. It is the purpose of the inner iterations to determine h_i, given h_{i+1} and h_{i-1}. Use is made of the fact that $\bar{S}_{i0}$ and $\bar{S}_{i1}$ are monotonically increasing functions of h_i which intersect at one nonzero point. Starting with an interval of h_i bounded by 0 and some value which is certainly larger than the correct h_i and calculating $\bar{S}^z{}_{i1}$ and $\bar{S}^z{}_{i1}$ for h_i at the center of the interval, one can determine within which half of the interval the correct h_i lies by noting whether $\bar{S}^z{}_{i0}$ is greater or less than $\bar{S}^z{}_{i1}$ at the center. In this way h_i can be bracketed within successively smaller intervals and determined to any desired accuracy.

A computer program was written to perform these steps and to give for a given ϵ and film thicknesses, the h_i's and corresponding $\bar{S}_{0i}$.

III. RESULTS

The results of the calculations are indicated graphically in Figs. 1 and 2. Figure 1 shows the temperature dependence of the magnetization for each of the models discussed. In the spatially-dependent case, the center atom of the film is the one plotted. These latter models are seen to differ only slightly from the corresponding bulk cases, but the higher-order approximations have a very different temperature dependence and appreciably lower Curie Temperature. As the film thickness increases in the spatially-dependent cases, the curves rapidly approach those for the bulk case. The points

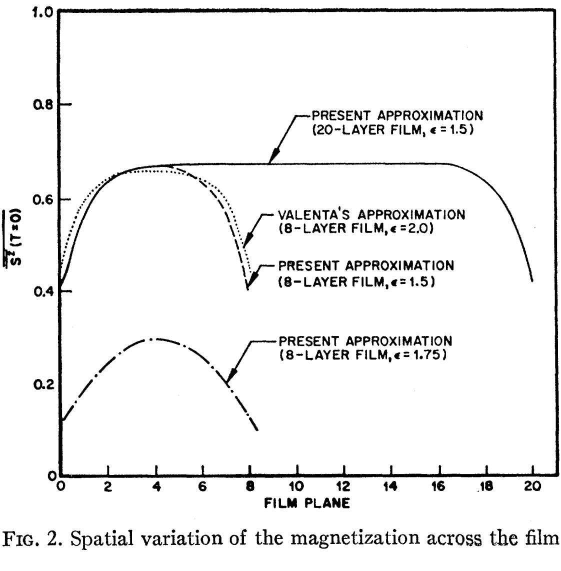

FIG. 2. Spatial variation of the magnetization across the film.

shown for the approximation of this paper are for a film thickness of eight layers. A point for a 20-layer film at $k/T_c = 1.5$ lies directly on the bulk curve. The remaining curve in Fig. 1 illustrates the sensitivity of the BPW model to the method of choosing the molecular field. In the molecular-field model, the field acting on a given spin is said to be equal to the number of nearest neighbors multiplied by the average spin projection of one of them. An analogous approach in the BPW approximation would be to choose the field acting on a spin to be the sum of the products for each plane of the number of nearest neighbors in the plane which are not treated exactly and the average spin projection in that plane. The results of doing this are shown in the curve mentioned above. That the BPW criterion is the correct one is indicated by the agreement it gives with the results of a calculation by Opechowski using an independent method, but the implied sensitivity to the method of choosing h is somewhat disconcerting.

Figure 2 shows the spatial profile of the magnetization for the present approximation at two temperatures and for two film thicknesses. The rate of rise of the magnetization to its interior value is seen to depend very little on the film thickness. One profile is also shown for Valenta's molecular-field model at a temperature chosen to give an interior value of the magnetization equal to that in one of the other curves. The falloff is seen to be somewhat less rapid in this model.

ACKNOWLEDGMENT

The impetus for the present work was provided by an unpublished calculation of J. I. Kaplan done independently of Valenta but using essentially the same approximation. The author wishes to thank Professor Kaplan for showing him his work.

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Anomalous Thermal Expansion and Magnetostriction of Single-Crystal Dysprosium

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(Received 6 November 1964)

The temperature and field dependences of the magnetostriction and thermal expansion of single-crystal dysprosium metal were measured in the paramagnetic, spiral, and ferromagnetic regions. In the paramagnetic temperature range from the Néel point to room temperature, the thermal expansion is normal and the six lowest order magnetostriction coefficients vary as H^2. As the temperature is lowered and the spins align, the magnetostriction becomes immense (0.62% at 80°K) and terms in the thermal expansion attributed to thermal vibrations are dwarfed by those arising from the magnetoelastic energy ($\approx 350\ \mathrm{cm}^{-1}\ \mathrm{atom}^{-1}$). Consequently, large discontinuities in the length of the hexagonal a and c axes occur when the spiral spin structure changes into the aligned configurations. Because the basal plane is the plane of easy magnetization in dysprosium, the basal-plane shearing magnetostriction is measurable over a wide range in temperature. Good agreement for this coefficient is found between the measured magnetostriction and that predicted by the single-ion magnetoelastic coupling theory $[\lambda(T)=\lambda(0)\hat{I}_{5/2}(\mathcal{L}^{-1}(m))]$. The magnetostriction is proportional to m^3 at low temperatures and to $3m^2/5$ at high temperatures with the exceptionally large proportionality constant of $\lambda(0)=8.5\times10^{-3}$.

I. INTRODUCTION

THE Curie point ($T_C = 85°\mathrm{K}$) and Néel point ($T_N = 178°\mathrm{K}$) of dysprosium were established by Trombe[1] and have been amply confirmed by others.[2] Magnetic measurements on single crystals by Behrendt, Legvold, and Spedding[3] have shown that in the ferromagnetic state the magnetization is firmly fixed in the hexagonal basal plane (00·1) and at low temperatures has an increasingly large anisotropy in the plane with the easy direction parallel to the a axis. Wilkinson *et al.*[4] observed that a spiral structure exists between 85 and 178°K and that the magnetization is always in the basal plane but changes in direction from one plane to the next with a turn-angle increasing almost linearly with temperature from 27° to 43° per layer.

The magnetostriction of polycrystalline Dy has been measured by Belov *et al.*[5] and by Lee and Alberts,[6] who found unusually high values. Even higher values, ob-

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