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Surface effects on the paramagnetic phase transitions of uniaxial antiferromagnets

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Abstract. We determine the bulk and surface canted-paramagnetic phase boundary of uniaxial antiferromagnets as a function of temperature for a semi-infinite system. Within the Green-function formalism, we show that the canted-paramagnetic critical field at the surface, which depends on the ratio of the surface to bulk exchange coupling, is larger than that corresponding to the bulk. This critical field at the surface does not follow a $T^{3/2}$ Bloch law, but instead decreases linearly with temperature. At a given temperature, which also depends on the ratio of the surface to bulk exchange coupling, the surface critical field becomes identical to that of the bulk.

1. Introduction

A static magnetic field applied along the easy axis of a low-anisotropy antiferromagnet may induce, at low temperatures, a continuous phase transition between a spin-flop and a paramagnetic phase. The temperature behaviour of this canted-paramagnetic boundary has been the subject of several experimental [1–4] and theoretical [5–8] investigations. On the other hand surface magnetism has been a field of growing interest in recent years.

From a experimental point of view the observation [9, 10] that some rare-earth materials exhibit a magnetically ordered phase over a paramagnetic bulk renewed interest in the magnetic surface phase transition. To probe the magnetization of surface layers sophisticated experimental techniques have been used, such as spin-polarized low-energy electron diffraction [11]. These transitions have also been investigated theoretically: series expansions [12], Monte Carlo simulations [13, 14], renormalization-group techniques [15, 16] and Green functions [17, 18].

Another interesting phenomenon concerns the antiferromagnetic phase transition induced by a field in uniaxial antiferromagnets. It is well known that the softening of the surface magnons occurs in a smaller field than that of the thermodynamic phase transition between the antiferromagnetic and spin-flop phases [19, 20]. The same behaviour appears in semi-infinite magnetic Fe/Gd superlattices whose interfacial coupling is antiferromagnetic [21]. When the external magnetic field is increased from zero one surface mode is driven soft, and a surface phase transition appears at a field value which is about five times lower than that necessary to cause a bulk phase transition.

We know that an antiferromagnetic system in its high-field phase, paramagnetic, has only one sublattice, and can be handled as if it were a ferromagnet. By using a Green-function formalism we can determine the dispersion relations for the surface spin waves as a function of the field and temperature. We show that, like the bulk spin waves, the spectrum

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of surface spin waves has a minimum at the corners of the corresponding Brillouin zone. If the field is decreased from high values these surface modes become soft, indicating a surface phase transition to a spin-flop phase. This critical field is greater than that corresponding to the bulk critical field and depends on the ratio of the surface and bulk exchange couplings. Besides, the surface critical field decreases linearly with the temperature up to a given value of temperature that depends of the ratio of the surface and bulk exchange couplings. Above this critical ratio the bulk and surface critical fields become identical. In section 2 we present the model Hamiltonian and calculations performed within the Green-function formalism. Finally, in section 3 we present the results and discussions for the paramagnetic phase transitions, and our conclusions.

2. Model Hamiltonian and calculations

We consider the following model Hamiltonian on a semi-infinite simple cubic lattice with a (010) free surface:

$$\mathbf{H} = \sum_{\langle i,j \rangle} [J_{ij}(1-\epsilon_{ij})(S_i^x S_j^x + S_i^y S_j^y) + J_{ij} S_i^z S_j^z] - g\mu_B H \sum_i S_i^z \tag{1}$$

where J_{ij} represents the antiferromagnetic exchange interaction between all pairs $\langle ij \rangle$ of nearest-neighbouring sites. We choose the following values for the parameters J_{ij} and ϵ_{ij}. If the sites i and j are at the surface plane ($l = 0$), we take $J_{ij} = J_s$ and $\epsilon_{ij} = \epsilon_s$. For all other neighbouring sites, $J_{ij} = J$ and $\epsilon_{ij} = \epsilon$. H is the magnetic field applied parallel to the (010) plane. The $S_i^{x,y,z}$ are the components of the spin-$\frac{1}{2}$ operators. The value $\epsilon = 0$ describes a Heisenberg model while $\epsilon = 1$ represents an Ising model. We assume that the spins will be oriented preferentially parallel to the surface, so that demagnetizing fields can be disregarded. We employ the Green-function formalism, within RPA decoupling, to determine the dispersion relations of the surface spin waves. The equations of motion for the Fourier transform of the Green functions $\langle\langle S_l^+(t); S_m^-(t')\rangle\rangle$ are given by

$$\left[E + \sum_i J_{il}\langle S_i^z\rangle - g\mu_B H\right]\langle\langle S_l^+; S_m^-\rangle\rangle_E - \langle S_l^z\rangle \sum_i (1-\epsilon_{il}) J_{il}\langle\langle S_i^+; S_m^-\rangle\rangle_E = \frac{1}{\pi}\langle S_l^z\rangle \delta_{lm} \tag{2}$$

where $\langle\langle S_l^+; S_m^-\rangle\rangle_E$ stands for the Fourier transforms of the Green functions. We have also assumed that the mean value $\langle S_l^z\rangle$ is the same for all sites inside a given plane l, that is,

$$\langle S_l^z\rangle = \langle S_l^z\rangle \tag{3}$$

where $l = 0$ represents the surface plane, $l = 1$, the next inner plane, and so on. For $l \geqslant 2$ we have also taken $\langle S_l^z\rangle = \langle S^z\rangle_b$, where $\langle S^z\rangle_b$ stands for the bulk magnetization.

As our system exhibits a translational symmetry parallel to the (010) plane, we take the Fourier transform of the Green function, $G(\boldsymbol{K}, E)$, where the wave vectors $\boldsymbol{K}$ belong to the two-dimensional Brillouin zone of a square lattice. Finally, the Green functions can be determined by the following matrix equation:

$$[\Omega \mathbf{G}]_{lm} = (1/\pi)\langle S_l^z\rangle \delta_{lm} \tag{4}$$

where Ω is given by

$$\Omega = \begin{pmatrix} 2t+\alpha_{00} & \Omega_{01} & 0 & 0 & 0 & 0 & \dots \\ \Omega_{10} & 2t+\alpha_{11} & \Omega_{10} & 0 & 0 & 0 & \dots \\ 0 & \alpha & 2t+\alpha_{22} & \alpha & 0 & 0 & \dots \\ 0 & 0 & \alpha & 2t & \alpha & 0 & \dots \\ \vdots & \vdots & 0 & \alpha & 2t & \alpha & \dots \end{pmatrix} \tag{5}$$

and where we have defined that

$$\alpha_{00} = -[(1-\epsilon_s)\gamma_K - 1]zJ_s\langle S_0^z\rangle + J\langle S_1^z\rangle + [z(1-\epsilon)\gamma_K - (2+z)]J\langle S_2^z\rangle \tag{6}$$

$$\alpha_{11} = J\langle S_0^z\rangle - [(1-\epsilon)\gamma_K - 1]zJ\langle S_1^z\rangle + [z(1-\epsilon)\gamma_K - (1+z)\epsilon]J\langle S_2^z\rangle \tag{7}$$

$$\alpha_{22} = -(\langle S_2^z\rangle - \langle S_1^z\rangle)\epsilon J \tag{8}$$

$$\Omega_{01} = -(1-\epsilon)J\langle S_0^z\rangle \tag{9}$$

$$\Omega_{10} = -(1-\epsilon)J\langle S_1^z\rangle \tag{10}$$

$$\alpha = -(1-\epsilon)J\langle S_2^z\rangle \tag{11}$$

$$2t = E - [z(1-\epsilon)\gamma_K - (2+z)]J\langle S_2^z\rangle - g\mu_B H. \tag{12}$$

The structure factor for the (010) planes is given by $\gamma_K = \frac{1}{2}[\cos(aK_x)+\cos(aK_z)]$ where a is the lattice spacing. In order to calculate the layer magnetization it is first necessary to evaluate Ω^{-1}. This is given by

$$(\Omega^{-1})_{ll} = N_l(\xi)/D(\xi) \tag{13}$$

where

$$N_0(\xi) = \xi[\alpha_{22}\xi^3 + (\alpha^2 - \alpha\Omega_{10} + \alpha_{11}\alpha_{22})\xi^2 + \alpha^2(\alpha_{11}+\alpha_{22})\xi + \alpha^4] \tag{14}$$

$$N_1(\xi) = \xi[\alpha_{22}\xi^3 + (\alpha^2 + \alpha_{00}\alpha_{22})\xi^2 + \alpha^2(\alpha_{00}+\alpha_{22})\xi + \alpha^4] \tag{15}$$

and

$$D(\xi) = \sum_{i=0}^{5} a_i\xi^i \tag{16}$$

with

$$a_0 = \alpha^6 \tag{17}$$

$$a_1 = \alpha^4(\alpha_{00}+\alpha_{11}+\alpha_{22}) \tag{18}$$

$$a_2 = 2\alpha^4 - \Omega_{10}\alpha^3 + (\alpha_{11}+\alpha_{22})\alpha_{00} + \alpha_{11}\alpha_{22} - \Omega_{01}\Omega_{10} \tag{19}$$

$$a_3 = (\alpha_{00}+\alpha_{11}+\alpha_{22})\alpha^2 - \alpha_{00}\Omega_{10}\alpha - \alpha_{22}\Omega_{01}\Omega_{10} + \alpha_{00}\alpha_{11}\alpha_{22} \tag{20}$$

$$a_4 = \alpha^2 - \Omega_{10}\alpha + (\alpha_{00}+\alpha_{11})\alpha_{22} \tag{21}$$

$$a_5 = \alpha_{22}. \tag{22}$$

The values of ξ are determined by the equation

$$\xi^2 - 2t\xi + \alpha^2 = 0. \tag{23}$$

If $|t| \leqslant \alpha$ the roots are complex, and if we write t as $-\alpha\cos(aK_y)$, equation (12) gives us the bulk dispersion relation for magnons. On the other hand, if $|t| > \alpha$, the roots of equation (23) are real and only those for which $|\xi| < 1$ will have a physical meaning. The poles of the Green functions are given by the real roots of the equation

$$D(\xi_s) = 0, \tag{24}$$

The spectrum of the surface magnons is determined from the roots of the above equation with the restriction that $|\xi_s| < 1$. In this case we obtain the following expression for the surface magnons:

$$\nu_K = \xi_s - \alpha^2\xi_s^{-1} + [(1-\epsilon)z\gamma_K - (2+z)]J\langle S_2^z\rangle + g\mu_B H. \tag{25}$$

To calculate the values of ξ_s, we need first to determine the layer magnetization $\langle S_0^z\rangle$ and $\langle S_1^z\rangle$ and the bulk magnetization $\langle S^z\rangle_b$, which here is taken at the third layer. The layer magnetization is then written as

$$\langle S_{0,1}^z\rangle = \tfrac{1}{2}/(1+2\phi_{0,1}) \tag{26}$$

where

$$\phi_{0,1} = -\frac{2}{\pi}\left(\frac{a}{2\pi}\right)^2 \int \mathrm{d}K \left[\int_{-\alpha}^{\alpha} \mathrm{d}t\ \mathrm{Im}\left(\frac{N_{0,1}(\xi)}{D(\xi)}\right)\Big/(\mathrm{e}^{\beta\nu}-1) + \frac{\pi}{2}\sum_{\gamma}\frac{N_{0,1}(\xi_\gamma)}{D'(\xi_\gamma)}\frac{(\alpha^2-\xi_\gamma^2)}{\xi_\gamma^2(\mathrm{e}^{\beta\nu}-1)}\right] \tag{27}$$

ξ_γ being the real roots of $D(\xi_\gamma)$ and $D'(\xi_\gamma)$ its derivative calculated at the point $\xi = \xi_\gamma$.

In our calculations we first must determine the bulk magnetization as a function of temperature and magnetic field, that is,

$$\langle S^z\rangle_b = \tfrac{1}{2}/(1+2\phi) \tag{28}$$

where

$$\phi = \frac{1}{N}\sum_q (\mathrm{e}^{\beta\omega_q} - 1) \tag{29}$$

and

$$\omega_q = -zJ\langle S^z\rangle_b[1-(1-\epsilon)\Gamma_q] + g\mu_B H \tag{30}$$

is the spectrum of the bulk magnons. Here the q values run over the first Brillouin zone of a simple cubic lattice ($z = 6$) with structure factor Γ_q.

The equations (26) and (27) are solved self-consistently for $\langle S_0^z\rangle$ and $\langle S_1^z\rangle$ for each pair of values of temperature and magnetic field. In this way we are able to determine the spectrum of the bulk and surface magnons as a function of temperature and magnetic field for this semi-infinite anisotropic Heisenberg model.

The magnitude of the canted-paramagnetic critical field is determined by the limit of stability of the paramagnetic phase, namely by the equations $\omega_{q_0}(T, H) = 0$ and $\nu_{K_0}(T, H) = 0$, where q_0 and K_0 are, respectively, wave vectors at the corners of the first Brillouin zone of simple cubic and square lattices.

3. Results

As an example, we show in figure 1 the surface magnon spectrum for two values of the magnetic field. We have taken $\epsilon_s = 0.40$, $\epsilon = 0.40$, $J_s/J = 1.50$ and $\tau = k_B T/6J = 0.010$ (low-temperature region). As the magnetic field decreases from the paramagnetic phase, the surface magnons move to lower frequencies, and the minimum value occurs at the corners of the first Brillouin zone. Eventually, this surface mode is driven to zero at a given critical field. The same reasoning applies to the bulk modes.

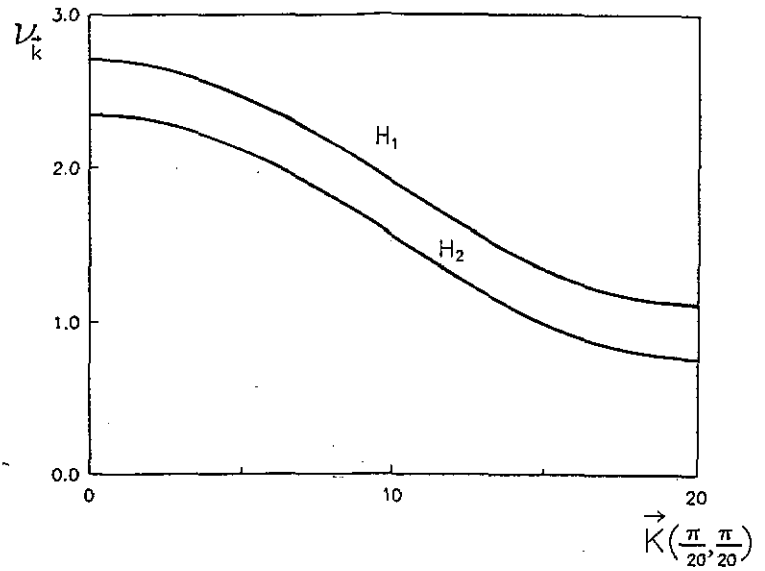

Figure 1. Surface magnon spectrum for two values of the reduced magnetic field $H(= g\mu_B H/6JS)$. We have $\epsilon_s = \epsilon = 0.40$, $J_s/J = 1.50$ and $\tau = k_B T/6SJ = 0.010$; $H_1 = 0.53$ and $H_2 = 0.49$.

In figure 2 we exhibit the critical field where the surface and bulk modes are driven to zero as a function of temperature. We observe that the surface canted-paramagnetic phase transition occurs at a field which is larger than the corresponding field in the bulk material. The difference between these critical fields is larger at $T = 0$ (for the values considered it is about 12%) and decreases up to a given temperature (τ_{sb}) where they become identical. While the canted-paramagnetic critical field of the bulk decreases with temperature according to the celebrated $T^{3/2}$ Bloch law, the surface critical field decreases linearly with temperature. This linear behaviour was obtained through a careful analysis of our numerical data at low temperatures. We have seen that the linear dependence of the surface critical field is the best fitting to our numerical data. This is a surprising result because a linear behaviour is expected only for a strictly two-dimensional system, and in our case we are considering a semi-infinite one. We call attention to a related behaviour existing between surfaces and semi-infinite systems. For a ferromagnetic system when both the surface and the bulk are described by a Heisenberg model, there is no long-range surface magnetic order over a paramagnetic bulk, whatever the values of the ratio between surface and bulk exchange couplings [22]. Although there is no rigorous proof of this behaviour for

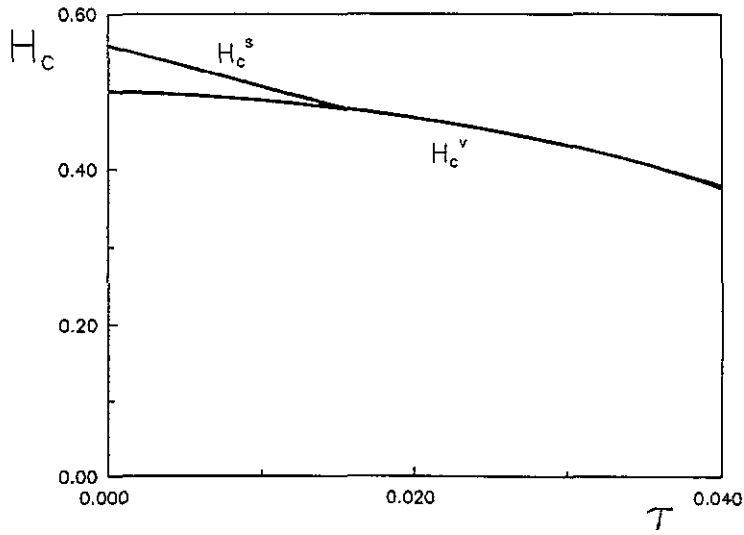

Figure 2. Surface (H_c^s) and bulk (H_c^b) canted-paramagnetic critical fields as a function of temperature. We have $\epsilon_s = \epsilon = 0.40$ and $J_s/J = 1.50$. The surface critical field decreases linearly with temperature and the bulk follows the $T^{3/2}$ Bloch law.

a semi-infinite system, this is analogous to the well known result of Mermin and Wagner [23], demonstrated for a two-dimensional Heisenberg model.

It is interesting to note that between the surface and the bulk phase transition the system exhibits a surface spin-flop state over a bulk paramagnetic state. Due to our approximation that the third plane is chosen as belonging to the bulk, this surface spin-flop state is localized in the first two surface planes. As we decrease the magnetic field after the surface transition is attained, the canting angles of the first two planes increase until we reach the critical magnetic field of the bulk transition where the spin-flop state extends over all the planes in the system.

We have seen in figure 2 that the surface paramagnetic critical field decreases with temperature and becomes identical to the bulk critical field at a given temperature τ_{sb}. This temperature depends on the ratio of the surface and bulk exchange parameters. This can be seen in figure 3 where we have plotted this ratio as a function of temperature. At $T = 0$ this ratio is $J_s/J = 1.23$ for $\epsilon = \epsilon_s = 0.40$. This ratio is also a smooth increasing function of temperature.

These results are interesting because we have found a critical surface field greater than that of the bulk across a boundary where the absence of hysteresis is well established. Here, the limits of stability of the spin-flop and paramagnetic phases occurs at the same field, different from that determined for the antiferromagnetic phase boundary [6]. We would like to stress that the same behaviour is also observed for other values of the anisotropy parameters ϵ and ϵ_s. Therefore, the results are not affected by the fact that we have taken only two independent planes above the bulk. For instance, when the number of perturbed planes varies from two to three, the increase in the layer magnetizations is about 1%.

In conclusion we expect that new measurements on the canted-paramagnetic phase boundary of antiferromagnetic systems can be performed to test the validity of our arguments. We think this is really possible because there are in the literature many results

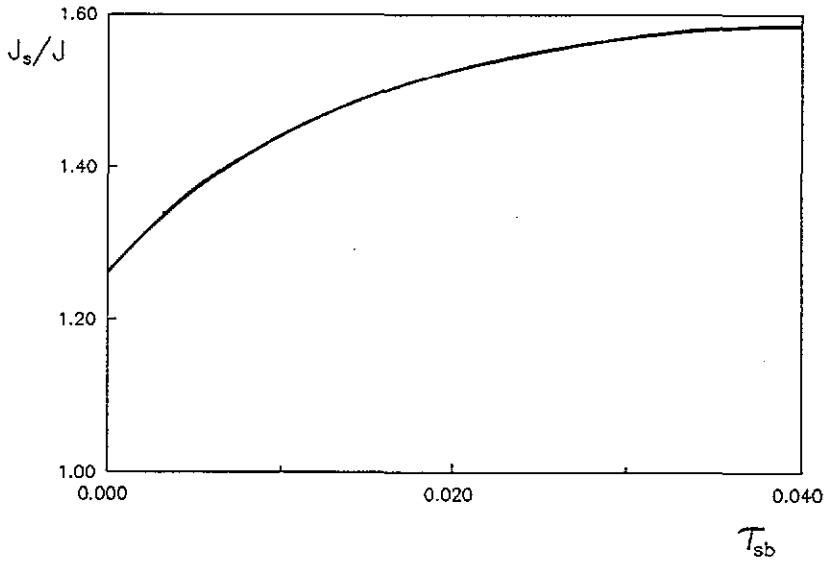

Figure 3. Behaviour of the ratio of the surface to bulk exchange coupling as a function of τ_{sb}, the temperature at which the surface and bulk canted-paramagnetic critical fields become identical.

concerning the bulk spin-flop paramagnetic phase boundary of anisotropic antiferromagnets. For instance, the antiferromagnet $NiCl_2 \cdot 4H_2O$ has a bulk canted-paramagnetic critical field [4] at $T = 0$ equal to 68.35 kOe. If the ratio of the surface to bulk exchange coupling in this antiferromagnet were larger than that determined in figure 3, at $\tau_{sb} = 0$, we easily could observe a surface paramagnetic phase transition. For instance, if $J_s/J = 1.25$, the critical field at the surface would be 1% larger than that of the bulk, that is, more or less 7 kOe for $NiCl_2 \cdot 4H_2O$, which is easily measurable in experiments.

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References

[1] Rives J E and Benedict V 1975 *Phys. Rev.* B **12** 1908
[2] Rives J E and Bathia S N 1975 *Phys. Rev.* B **12** 1920
[3] Oliveira N F Jr, Paduan-Filho A, Salinas S R and Becerra C C 1978 *Phys. Rev.* B **18** 6165
[4] Becerra C C, Oliveira N F Jr, Paduan-Filho A, Figueiredo W and de Souza M V P 1988 *Phys. Rev.* B **38** 6887
[5] Anderson F B and Callen H B 1964 *Phys. Rev.* A **136** 1068
[6] Feder J and Pytte E 1968 *Phys. Rev.* **168** 640
[7] Figueiredo W and Salinas S R 1984 *Physica* B **124** 259
[8] Figueiredo W 1989 *J. Phys.: Condens. Matter* **1** 7433
[9] Weller D, Alvarado S F, Gudat W, Schröder K and Campagna M 1985 *Phys. Rev. Lett.* **54** 1555
[10] Rau C, Jin C and Robert M 1988 *J. Appl. Phys.* **63** 3667

[11] Celotta R J and Pierce D T 1986 *Science* **234** 249
[12] Binder K and Hohenberg P C 1971 *Phys. Rev.* B **9** 2194
[13] Binder K and Landau D P 1984 *Phys. Rev. Lett.* **52** 318
[14] Landau D P and Binder K 1990 *Phys. Rev.* B **41** 4786
[15] Mariz A M, Costa U M S and Tsallis C 1987 *Europhys. Lett.* **3** 27
[16] Ohno K and Okabe Y 1989 *Phys. Rev.* B **39** 9764
[17] Selzer S and Majlis N 1983 *Phys. Rev.* B **27** 544
[18] Endo Y and Ayukawa T 1989 *J. Phys. Soc. Japan* **58** 2515
[19] Mills D L 1968 *Phys. Rev. Lett.* **20** 18
[20] Keffer F and Chow H 1973 *Phys. Rev. Lett.* **31** 1061
[21] LePage J G and Camley R E 1990 *Phys. Rev. Lett.* **65** 1152
[22] de Moraes J N B and Figueiredo W 1991 *Phys. Lett.* **157A** 237
[23] Mermin N D and Wagner H 1966 *Phys. Rev. Lett.* **17** 1133