Surface Effects in Magnetic Crystals near the Ordering Temperature*

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A form of the Landau-Ginsberg equations applicable to semi-infinite magnetic crystals is derived from the molecular-field theory. We consider both the Heisenberg antiferromagnet and the Heisenberg ferromagnet. We find simple analytic expressions that describe the temperature dependence of the order parameter in the surface region near the ordering temperature. In both cases we find that the order parameter in the surface vanishes linearly with temperature as the ordering temperature is approached from below. This result is in good agreement with the temperature variation of the sublattice magnetization in the surface of antiferromagnetic NiO inferred from the low-energy-electron-diffraction (LEED) data of Palmberg and co-workers, for the entire range of temperatures studied ($0.8T_N < T < T_N$). We find that one cannot use the existing LEED data to determine the value of the exchange constants in the surface layer without a measurement of the absolute value of the sublattice magnetization or measurements over a wider range of temperatures. This conclusion differs from that reached in an earlier study based on a numerical solution of the molecular-field equations. We also examine the behavior of the static spin correlation function $\langle S_z(\vec{l})S_z(\vec{l}')\rangle$ in the paramagnetic state, when the sites $\vec{l}$ and/or $\vec{l}'$ lie near the surface. We find that there should be no magnetic critical scattering of low-energy electrons from the surface, as the ordering temperature is approached from above. The correlation length for spins in or near the surface remains the order of a lattice constant, even at the ordering temperature for both the ferromagnet and the antiferromagnet.

I. INTRODUCTION

The effect of a surface on the excitation spectrum and the thermodynamic properties of the Heisenberg ferromagnet and Heisenberg antiferromagnet has been discussed in a number of recent papers.[1] These investigations have been concerned with the low-temperature regime, where spin-wave theory is applicable. In the presence of the surface, one finds a new branch of the excitation spectrum associated with surface spin waves under a variety of conditions. These are waves which propagate parallel to the surface, but the spin motion associated with the mode is localized near the surface. The mean spin deviation is found to be larger near the surface than in the bulk, and the specific heat of the crystal is enhanced by a term proportional to the surface area. (If pinning fields are present in the surface, then the mean spin deviation near the surface and the specific heat are depressed.) Contributions to the change in specific heat and in the mean spin deviation near the surface come about because of the presence of the surface waves and because the eigenfunctions and frequency distribution of the bulk modes are altered by the presence of the surface.

The purpose of this paper is to discuss the effect of the surface on the properties of the Heisenberg antiferromagnet and ferromagnet, when the material is close to the ordering temperature. We begin with the molecular-field theory applied to the semi-infinite crystal placed in a static spatially varying magnetic field. From these equations we derive a form of the Landau-Ginsberg equation supplemented by a boundary condition at the surface. This equation is used to study the dependence of the magnetization on temperature and distance from the surface for temperatures below the ordering temperature. We also present a discussion of certain features of the response of the semi-infinite material to an external magnetic field. From this analysis, one can extract the form of the static spin correlation function $\langle S_z(\vec{l})S_z(\vec{l}')\rangle$ when $\vec{l}$ and/or $\vec{l}'$ are near the surface. We present a detailed discussion of the form of the theory for a model of a semi-infinite Heisenberg antiferromagnet, with two sublattices in the surface layer. We also give the equations that apply to the semi-infinite ferromagnet, and we indicate how the results for the antiferromagnet may be applied to this case by making the appropriate modifications in the formulas.

For the antiferromagnetic geometry mentioned above, we find that as the Néel temperature T_N is approached from below, the sublattice magnetization in the surface layer vanishes as $T_N - T$. This is in good accord with the behavior of the sublattice magnetization inferred from low-energy-electron-diffraction (LEED) data on the antiferromagnet NiO, as we shall see. The magnetization in the surface of a ferromagnet is also predicted to vanish linearly with the temperature as the Curie temperature is approached from below. These temperature dependences, which are appropriate

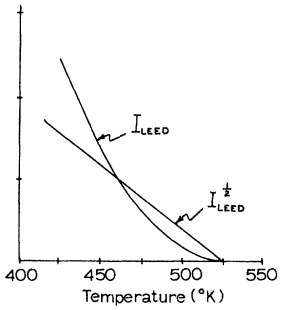

FIG. 1. Temperature dependence of the LEED intensity associated with Bragg scattering from the antiferromagnet order present in the surface of NiO. The data are taken from Ref. 2. We also plot the square root of the LEED intensity as a function of temperature.

to the regime $T_N - T \ll T_N$, are unaffected by the softening of exchange constants in the surface layer. If the exchange constants in the surface layer are reduced, then the magnitude of the order parameter at a given temperature is lowered, but the temperature dependence remains unaffected.

DeWames and Wolfram[2] have also presented calculations of the temperature dependence of the sublattice magnetization in the surface layer of an antiferromagnet. It is difficult to compare our analytic approach with their work, since they present their results only in graphical form. Furthermore, no information is supplied about the assumptions or techniques employed in performing the molecular-field calculations. One expects the LEED intensity I_{LEED} associated with the antiferromagnetic Bragg scattering to be proportional to the square of the sublattice magnetization $\langle S_z \rangle|_{\mathrm{surf}}$ in the surface layer when $T < T_N$. DeWames and Wolfram present a series of curves that give the temperature dependence of $\langle S_z \rangle^2|_{\mathrm{surf}}$ throughout the complete temperature range $0 < T < T_N$ for various values of the exchange constant in the surface layer. It is argued by these authors that the qualitative shape of $\langle S_z \rangle^2|_{\mathrm{surf}}$ as a function of temperature inferred from the LEED data can only be obtained if the exchange constant in the surface layer is much smaller than that appropriate to the bulk crystal. We reproduce the temperature dependence of I_{LEED} observed experimentally in NiO in Fig. 1 of the present paper.

It is important to note that the data extends only over a narrow temperature near T_N. The Néel temperature of NiO is 525 °K, and the data extend over the range 410–525 °K. If one examines the theoretical results presented by DeWames and Wolfram, one sees that in all cases considered they find $\langle S_z \rangle^2|_{\mathrm{surf}}$ to vanish linearly as $T \to T_N$. In particular, for the case where the exchange in the surface is half that of the bulk, their plot of $\langle S_z \rangle^2|_{\mathrm{surf}}$ appears to vary approximately in a linear fashion with T over the entire range of temperatures covered by the data. On the other hand, as one can see from Fig. 1, the data strongly suggest that I_{LEED}, and hence $\langle S_z \rangle^2|_{\mathrm{surf}}$, has a slope that vanishes as $T \to T_N$. Furthermore, the plot of I_{LEED} against temperature exhibits pronounced curvature throughout the region examined experimentally. Thus we feel that the theoretical results given by DeWames and Wolfram produce behavior of $\langle S_z \rangle^2|_{\mathrm{surf}}$ near the Néel temperature that appears to differ significantly from the data.

As mentioned above, we find that $\langle S_z \rangle|_{\mathrm{surf}}$ should vanish as $T_N - T$ as T_N is approached from below. The temperature dependence exhibited by $\langle S_z \rangle|_{\mathrm{surf}}$ near T_N should be independent of the amount by which the surface exchange is softened, although the magnitude of $\langle S_z \rangle|_{\mathrm{surf}}$ at any temperature decreases with decreasing exchange in the surface layer. Our theory predicts that the square root of the LEED intensity, $I_{\mathrm{LEED}}^{1/2}$, should thus vanish linearly with T, as T_N is approached from below. In Fig. 1 we have also plotted the experimental values of $I_{\mathrm{LEED}}^{1/2}$ against temperature. To within graphical accuracy, we find $I_{\mathrm{LEED}}^{1/2}$ is indeed proportional to $T_N - T$ throughout the temperature range studied experimentally. Since the experimental data is confined to the range of temperatures $0.8 T_N < T < T_N$ close to the Néel temperature, it appears as if only the limiting behavior of $\langle S_z \rangle|_{\mathrm{surf}}$ for small $T_N - T$ is observed. In view of our earlier remarks, this means that one cannot obtain information from the existing LEED data about the exchange constants in the surface layer, unless an absolute measurement of $\langle S_z \rangle|_{\mathrm{surf}}$ is available, or the data is extended to a wider range of temperatures. We feel that the parabolic shape of the graph of I_{LEED} against temperature observed in the experiment on NiO is to be expected quite generally, and is not a consequence of a special numerical value assumed by the exchange constants in the surface layer.

In Sec. II of the paper, we derive the form of the Landau-Ginsberg equations and the boundary condition on the order parameter appropriate to the semi-infinite antiferromagnet, with a surface layer that contains two sublattices. In Sec. III, we apply the equations to the discussion of the temperature dependence of the sublattice magnetization in the surface layer of such a crystal, and to its variation with distance from the surface. We also calculate the static spin correlation function $\langle S_z(\vec{l}) S_z(\vec{l}') \rangle$, and study its behavior when $\vec{l}$ and/or $\vec{l}'$ are near the surface. We find that there should be no critical scattering of low-energy electrons from the surface as the ordering temperature is approached from above since the static correlation length between spins in or near the surface remains the order of a lattice constant, even at the Néel temperature. In Sec. IV, we exhibit the form of the Landau-Ginsberg equations for the semi-infinite ferromagnet. We indicate that the results of Sec. III may also be applied to the ferromagnet, and the response of the semi-infinite ferromagnet to a uniform applied field is discussed for the case

where the temperature is near the Curie temperature.

We stress that all of the results derived in this paper assume the validity of the molecular-field theory. The description of the material we obtain is thus a very approximate one, and may break down when T is very close to the ordering temperature. The agreement between the temperature dependence of the magnetization in the surface layer of NiO inferred from the LEED data and the present theory suggests that the description of the surface properties of magnetic materials obtained from the molecular-field theory provides a good qualitative picture of the behavior of the surface region.

II. LANDAU-GINSBERG EQUATIONS AND BOUNDARY CONDITIONS AT THE SURFACE

As stated in the preceding section, we shall present a derivation of the form of the Landau-Ginsberg equations and the boundary condition to be applied to the order parameter at the surface for a specific model of an antiferromagnetic crystal. Consider an antiferromagnet constructed from two interpenetrating fcc sublattices. The crystal structure is thus taken to be the NaCl structure, and we label the sublattice with spins directed upward in the z direction as the A sublattice, with the sublattice that contains spins directed downward labeled the B sublattice. Each A spin in the bulk of the crystal interacts with its six nearest neighbors on the B sublattice via an isotropic Heisenberg exchange interaction J. The sign convention is such that J is positive when the interaction has antiferromagnetic character. Next, we presume that the crystal has a (110) surface. The surface layer thus consists of a face-centered square lattice of A spins, and a similar lattice of B spins. The spins in the surface layer are coupled by an exchange interaction $J_s = J - \Delta J$ that differs from the value appropriate to the bulk. Notice that we choose a sign convention such that when ΔJ is positive, the exchange in the surface layer is less than that of the bulk.

Suppose a magnetic field of strength $H_A(\vec{l})$ is applied along the z direction to the site $\vec{l}$ of sublattice A. We consider the general case where the (static) applied field may vary from site to site. One may compute the expectation value $\langle S_z^A(\vec{l})\rangle$ of the z component of the spin from the molecular-field theory by means of the following relation:

$$\langle S_z^A(\vec{l})\rangle = S B_s\left(\frac{g\mu_B H_A(\vec{l})}{k_B T} - \frac{J}{k_B T}\sum_{\vec{\delta}}\langle S_z^B(\vec{l}+\vec{\delta})\rangle\right). \tag{1}$$

We assume for the moment that the site $\vec{l}$ lies well within the crystal. In Eq. (1), $g\mu_B$ is the Landé g factor multiplied by the Bohr magneton, k_B and T are Boltzmann's constant and the absolute temperature, S is the spin of the magnetic ions, and $B_s(x)$ is the Brillouin function

$$B_s(x) = \left(1+\frac{1}{2S}\right)\coth(S+\tfrac{1}{2})x - \frac{1}{2S}\coth(\tfrac{1}{2}x), \tag{2a}$$

$$B_s(x) = \tfrac{1}{3}(S+1)\{x - \tfrac{1}{15}[S(S+1)+\tfrac{1}{2}]x^3 + \cdots\}. \tag{2b}$$

Finally, in Eq. (1) the sum over $\vec{\delta}$ ranges over the six B sites that form the nearest neighbors of the A spin.

We introduce the reduced temperature

$$\tau = T/T_N \quad ,$$

where the Néel temperature $T_N = 2JS(S+1)$ for the present model. We also measure the magnetic field in units of $k_B T_N$ by introducing the dimensionless quantity

$$h_A(\vec{l}) = (g\mu_B/k_B T_N) H_A(\vec{l}) .$$

The order parameters for the A and B sublattices are defined by the relations

$$\eta_{A,B}(\vec{l}) = \langle S^z_{A,B}(\vec{l})\rangle/S \quad .$$

Equation (1) may then be written

$$\eta_A(\vec{l}) = B_s\left(\frac{h_A(\vec{l})}{\tau} - \frac{1}{2\tau(S+1)}\sum_{\vec{\delta}}\eta_B(\vec{l}+\vec{\delta})\right). \tag{3a}$$

We shall confine our attention to the case where the disturbance induced by $h_A(\vec{l})$ varies slowly in space, on the scale of the lattice constant. This will be the case for temperatures near the Néel temperature T_N. Thus we regard $\eta_B(\vec{l})$ as a continuous function of $\vec{l}$ and write

$$\sum_{\vec{\delta}}\eta_B(\vec{l}+\delta) \cong 6\eta_B(\vec{l}) + a_0^2\nabla^2\eta_B(\vec{l}) , \tag{3b}$$

where a_0 is the distance between the A spin at $\vec{l}$ and one of the nearest neighbors on the B sublattice. Equation (3a) then becomes

$$\eta_A(\vec{l}) = B_s\left(\frac{h_A(\vec{l})}{\tau} - \frac{3}{\tau(S+1)}\eta_B(\vec{l}) - \frac{3a_0^2}{\tau(S+1)}\nabla^2\eta_B(\vec{l})\right). \tag{4}$$

We now suppose the amplitude of the external magnetic field and the disturbance $\eta_{A,B}(\vec{l})$ induced by it are small in amplitude. Upon expanding the Brillouin function in Eq. (4) in the power series [Eq. (2b)] valid for small arguments, and retaining only the terms first order in $h_A(\vec{l})$ and $\nabla^2\eta_B$, one finds a Landau-Ginsberg equation of the form

$$\tfrac{1}{6}a_0^2\nabla^2\eta_B(x) + \frac{1}{\tau}\eta_B(x) + \eta_A(x) - \beta\eta_B^3(x) = \frac{(S+1)}{3\tau}h_A(x) , \tag{5a}$$

where $\beta = \frac{3}{5}[S(S+1)+\frac{1}{2}]/(S+1)^2$ is a dimensionless constant with a value near unity.

If we consider a spin on the B sublattice in the bulk of the material, and we suppose the B sublattice is perturbed by a magnetic field $h_B(\vec{x})$ ap-

plied externally, we find a second equation linking $\eta_A(\vec{x})$ and $\eta_B(\vec{x})$ to the external field:

$$\tfrac{1}{6}a_0^2\nabla^2\eta_A(\vec{x})+\frac{1}{\tau}\eta_A(\vec{x})+\eta_B(\vec{x})-\beta\eta_A^3(\vec{x}) = \frac{(S+1)}{3\tau}h_B(\vec{x}) . \quad (5b)$$

In order to apply Eqs. (5) to the semi-infinite medium, one needs a boundary condition on the functions η_A, η_B at the crystal surface. We presume the surface lies in the x-y plane, and that the crystal occupies the half space $x>0$. Consider the molecular field seen by a spin in the surface layer on the A sublattice. If $J(\vec{\delta})$ is the stength of the exchange coupling between this spin and its neighbor on the B sublattice removed by the distance $\vec{\delta}$, one has

$$\sum_{\vec{\delta}}\frac{J(\vec{\delta})}{J}\eta_B(\vec{1}+\vec{\delta}) = \left(5\eta_B-4\Delta\eta_B+a_0\frac{\partial\eta_B}{\partial z}+(1-\Delta)a_0^2\nabla_{\parallel}^2\eta_B+\frac{a_0^2}{z}\frac{\partial^2\eta_B}{\partial z^2}\right)_{z=0},$$

where we define the parameter $\Delta=\Delta J/J$, and $\nabla_{\parallel}^2=\partial^2/\partial x^2+\partial^2/\partial y^2$. Upon comparing this result with Eq. (3b), one sees that the Landau-Ginsberg equations may be applied throughout the crystal, including the surface layer, providing the boundary condition

$$(1+4\Delta)\eta_B+a_0^2\Delta\nabla_{\parallel}^2\eta_B+\frac{a_0^2}{6}\frac{\partial^2\eta_B}{\partial z^2}\bigg|_{z=0}=a_0\frac{\partial\eta_B}{\partial z}\bigg|_{z=0}$$

is imposed upon the solution. Since Eqs. (5) are valid only when the order parameter varies slowly over lengths the order of the lattice constant, the terms on the left-hand side of the equation proportional to $\nabla_{\parallel}^2\eta_B$ and $\partial^2\eta_B/\partial z^2$ will be ignored. The boundary condition then becomes

$$(1+4\Delta)\eta_B\big|_{z=0}=a_0\frac{\partial\eta_B}{\partial z}\bigg|_{z=0} . \quad (6a)$$

If one considers the molecular field experienced by a B spin in the surface, one finds the second condition

$$(1+4\Delta)\eta_A\big|_{z=0}=a_0\frac{\partial\eta_A}{\partial z}\bigg|_{z=0} . \quad (6b)$$

In the remaining sections of the paper, we apply Eqs. (5), supplemented by the boundary conditions in Eqs. (6), to describe the behavior of the semi-infinite antiferromagnet. Recall that these equations are derived upon assuming that the order parameters η_A, η_B are small compared to unity and vary slowly in space over distances the order of a lattice constant. Of course, the principal assumption we have employed is that molecular-field theory provides an accurate description of the temperature and spatial variation of the sublattice magnetization of the semi-infinite antiferromagnet near the ordering temperature.

III. APPLICATIONS OF THE THEORY

A. Spatial and Temperature Dependence of Magnetization below Néel Temperature

Suppose that the temperature $T<T_N$ ($\tau<1$) and also that no external magnetic fields are applied to the system. Then $h_A(\vec{x})=h_B(\vec{x})=0$. Equations (5) and the boundary condition exhibited in Eqs. (6) admit a solution with

$$\eta_A(\vec{x})=-\eta_B(\vec{x})\equiv\eta(\vec{x}) .$$

This solution of the equations describes the antiferromagnetic order present in the semi-infinite crystal below T_N. The function $\eta(\vec{x})$ satisfies the homogeneous nonlinear equation

$$\tfrac{1}{6}a_0^2\nabla^2\eta(\vec{x})+(1/\tau-1)\eta(\vec{x})-\beta\eta^3(\vec{x})=0 , \quad (7)$$

supplemented by the boundary condition, at $z=0$,

$$\eta=\frac{a_0}{1+4\Delta}\frac{\partial\eta}{\partial z} . \quad (8)$$

We find, for T near T_N, $\tau\cong 1$. Also, in the absence of an external field, $\eta(\vec{x})$ will depend only on z. Thus, Eq. (7) becomes

$$\frac{a_0^2}{6}\frac{\partial^2\eta}{\partial z^2}+(1-\tau)\eta(z)-\beta\eta^3(z)=0 . \quad (9)$$

Far from the surface, $\eta(z)$ will be independent of z and equal to the value η_∞ deduced from Eq. (9) with η independent of z:

$$\eta_\infty=(1-\tau)^{1/2}/\beta^{1/2} . \quad (10)$$

It is well known that the molecular-field theory predicts that in the bulk crystal the order parameter vanishes as $(T_N-T)^{1/2}$ as T approaches T_N from below.

We now write

$$\eta(z)=\eta_\infty f(z)$$

and measure distance in terms of the correlation length $\xi=a_0/[6(1-\tau)]^{1/2}$ by writing $z=\xi y$. Equations (8) and (9) then become

$$\frac{\partial^2 f}{\partial y^2}+f(y)-f^3(y)=0 , \quad (11)$$

where at $y=0$,

$$f=\frac{a_0}{(1+4\Delta)\xi}\frac{\partial f}{\partial y} . \quad (12)$$

It is not possible to obtain an exact solution of Eq. (11) with the boundary condition $f(y)\to 1$ as $y\to\infty$ and also the boundary condition at $y=0$ expressed by Eq. (12). However, an approximate solution valid near the critical temperature can be obtained. Near the critical temperature, $\xi\gg a_0$. Then, since one expects $\partial f/\partial y$ to be the

order of unity, one has

$$f(0)=\frac{a_0}{(1+4\Delta)\xi}\frac{\partial f}{\partial y}=\text{order of }\frac{a_0}{\xi}\ll 1.$$

Thus the function $f(0)$ will become very small at $y=0$, when T is near T_N. We introduce the function $f^{(0)}(y)$ that satisfies Eq. (11) with the boundary conditions

$$f^{(0)}(0)=1,\quad f^{(0)}(\infty)=1\ .$$

The exact solution of Eq. (11) with the boundary condition of Eq. (12) may then be written

$$f(y)=f^{(0)}(y)+f^{(1)}(y)\ ,$$

where, for T near T_N, $f^{(1)}(y)$ is small compared to $f^{(0)}(y)$. When $f^{(1)}\ll f^{(0)}$, $f^{(1)}$ may be obtained from the differential equation

$$\frac{\partial^2 f^{(1)}}{\partial y^2}+(1-3f^{(0)2})f^{(1)}=0\ , \tag{13}$$

where

$$f^{(1)}(0)=\frac{a_0}{(1+4\Delta)\xi}\frac{\partial f^{(0)}(0)}{dy}\ ,\quad f^{(1)}(\infty)=0\ . \tag{14}$$

In fact, if we are given the function $f^{(0)}(y)$ and only inquire about the value of the order parameter in the surface layer, then this quantity is given directly by Eq. (14) upon noting that $f(0)=f^{(0)}(0)+f^{(1)}(0)\equiv f^{(1)}(0)$. Thus, to obtain this limited amount of information, one need not solve Eq. (13). It may be shown that

$$f^{(0)}(y)=\tanh(y/\sqrt{2}\,).$$

Thus, when T is near T_N,

$$f^{(1)}(0)=\frac{a_0}{\sqrt{2}\,(1+4\Delta)\xi}=\frac{\sqrt{3}}{(1+4\Delta)}\left(\frac{T_N-T}{T_N}\right)^{1/2}. \tag{15}$$

The sublattice magnetization $\langle S_z\rangle|_{\text{surf}}$ in the surface is thus

$$\langle S_z\rangle|_{\text{surf}}=S\eta(0)=S\eta_\infty f^{(1)}(0)\ ,$$

or

$$\langle S_z\rangle|_{\text{surf}}=\frac{\sqrt{3}\,S}{\sqrt{\beta}\,(1+4\Delta)}\frac{T_N-T}{T_N}\ . \tag{16}$$

This is the result referred to in Sec. I. For temperatures near T_N, the sublattice magnetization in the surface is proportional to T_N-T in the molecular-field theory. If the exchange constants in the surface layer are softened ($\Delta>0$), then $\langle S_z\rangle|_{\text{surf}}$ is reduced in value, but the temperature dependence of $\langle S_z\rangle|_{\text{surf}}$ is unaffected. As remarked earlier, the LEED intensity is proportional to $\langle S_z\rangle^2|_{\text{surf}}$ below T_N. From Fig. 1, one sees that $I_{\text{LEED}}^{1/2}$, and consequently $\langle S_z\rangle^2|_{\text{surf}}$ in NiO, are proportional to T_N-T for $0.8T_N<T<T_N$. The parabolic form of I_{LEED} as a function of temperature is not a consequence of any particular value of the exchange appropriate to the surface layer as argued previously,[2] but is rather expected to be a general feature of the temperature dependence of the LEED intensity associated with Bragg scattering induced by antiferromagnetic order in the crystal surface. As remarked above, so long as only the limiting behavior exhibited in Eq. (16) is observed, one cannot obtain numerical values of the surface exchange without information about the absolute value of $\langle S_z\rangle|_{\text{surf}}$, or data over a wider range of temperatures.

If the surface exchange is stiffened ($\Delta<0$), then one sees that when Δ is larger than $\frac{1}{4}$ in magnitude, the right-hand side of Eq. (16) predicts that $\langle S_z\rangle|_{\text{surf}}$ is negative; indeed, for $\Delta=-\frac{1}{4}$, the surface magnetization is predicted to be infinite by Eq. (16). One may show that when $\Delta<-\frac{1}{4}$, the molecular-field theory predicts that the surface region will order antiferromagnetically at a temperature higher than the bulk Néel temperature T_N. As the temperature is lowered, the surface region orders at a temperature $T_N^{(s)}>T_N$; then, at T_N, the entire crystal orders, according to the molecular-field theory. We shall see how this feature enters the theory in Sec. IV. If $\Delta<-\frac{1}{4}$, the antiferromagnetic order in the region $T_N^{(s)}>T>T_N$ is confined to within one or two layers of surface, i.e., the order parameter decays to zero with a characteristic length the order of the lattice parameter a_0. (However, if Δ is very close to $-\frac{1}{4}$ in value, this characteristic length becomes long compared to a_0. This special situation is not of practical interest.) Since it is well known that true antiferromagnetic ordering cannot occur in two dimensions, it is doubtful that this surface antiferromagnetism would occur in a real crystal. The existence of this phase transition is most likely an artifact of the molecular-field theory which completely ignores the effect of fluctuations on the phase transition. However, this result suggests that if the surface exchange is appreciably larger than the bulk exchange, then well above T_N there may be long-range correlations between the spins in the surface layer, while the bulk correlation length remains the order of a_0. This possibility cannot be explored with the present theory however.

B. Spin Correlations above the Néel Temperature

In this section we calculate the form of the static spin correlation function $\langle S_z(\vec{l}\,')S_z(\vec{l})\rangle$ for the semi-infinite antiferromagnet, within the framework of the molecular-field theory developed in Sec. II.

The static correlation function will be computed by employing an argument similar to the one utilized by Friedel and de Gennes[3] in their discussion of the theory of spin-disorder scattering of conduction electrons in metals, and in a previous discussion of the properties of the semi-infinite ferromagnet.[4] Imagine that the crystal is in thermal equilibrium at some temperature $T>T_N$. Then the spin at

site $\vec{l}$ is pinned along the z direction, so that $\langle S_z(\vec{l})\rangle = +S$. Then the molecular-field theory is employed to compute $\langle S_z(\vec{l}')\rangle_{\vec{l}}$, where the subscript attached to the right-hand bracket denotes that the expectation value of $S_z(\vec{l}')$ is computed with the spin at site pinned in the manner just described. Then

$$\langle S_z(\vec{l}')S_z(\vec{l})\rangle = S\langle S_z(\vec{l}')\rangle_{\vec{l}} = S^2\eta(l';l)\,, \tag{17}$$

where in the last statement we write

$$\eta(\vec{l}',\vec{l}) = \langle S_z(\vec{l}')\rangle/S\,.$$

For the antiferromagnet, a slightly more explicit notation is required. Suppose we choose to pin in the z direction a spin at the site $\vec{l}$ of the A sublattice. Then we need to compute the pair of correlation functions $\langle S_z^A(\vec{l}')S_z^A(\vec{l})\rangle$ and $\langle S_z^B(\vec{l}')S_z^A(\vec{l})\rangle$. Also since we consider the properties of the semi-infinite medium, it is convenient to replace $\vec{l}$ and $\vec{l}'$ by the combinations $(\vec{l}_\parallel, l_z)$, $(\vec{l}'_\parallel, l'_z)$, where $\vec{l}_\parallel$ measures the position of $\vec{l}$ in the plane parallel to the surface, and l_z measures the distance of the site $\vec{l}$ from the surface. The correlation functions $\langle S^z_{A,B}(\vec{l}')S^z_B(l)\rangle$ are easily obtained from those of Eq. (17) by symmetry considerations.

If a spin on sublattice A is pinned in the $+z$ direction, then from the point of view of molecular-field theory, the system responds as if a magnetic field of strength $g\mu_B H_A = +JS$ is applied at the site $\vec{l}$ of the spin. In the continuum limit, such a field may be represented by inserting into Eqs. (5) the driving fields

$$h_A(\vec{x}) = [a_0^3/2(S+1)]\,\delta(\vec{x}-\vec{l})\,, \quad h_B(\vec{x}) = 0\,.$$

Since the order arises only from the presence of the driving field when $T > T_N$, the terms in $\eta^3(\vec{x})$ may be neglected in Eqs. (5). Thus the functions $\eta_{A,B}(\vec{x};l)$ satisfy

$$\tfrac{1}{6}a_0^2\nabla^2\eta_B(\vec{x};l) + (1/\tau)\eta_B(\vec{x};l) + \eta_A(\vec{x};l) = (a_0^3/6\tau)\,\delta(\vec{x}-\vec{l})\,, \tag{18a}$$

$$\tfrac{1}{6}a_0^2\nabla^2\eta_A(\vec{x};l) + (1/\tau)\eta_A(\vec{x};\vec{l}) + \eta_B(\vec{x};l) = 0\,. \tag{18b}$$

Recall the boundary conditions at $z=0$:

$$(1+4\Delta)\,\eta_{A,B}(\vec{x};\vec{l}) = a_0\frac{\partial\eta_{A,B}}{\partial z}(\vec{x};\vec{l})\,. \tag{19}$$

Introduce the "staggered magnetization"

$$s(\vec{x};\vec{l}) = \eta_A(\vec{x};\vec{l}) - \eta_B(\vec{x};\vec{l})\,.$$

Then $s(\vec{x};\vec{l})$ satisfies (for τ near unity)

$$-\nabla^2 s(\vec{x};\vec{l}) + (1/\xi^2)\,s(\vec{x};\vec{l}) = a_0\delta(\vec{x}-\vec{l})\,, \tag{20}$$

where, at $z=0$,

$$(1+4\Delta)s = a_0\frac{\partial s}{\partial z}\,. \tag{21}$$

We have introduced the correlation length $\xi = a_0/[6(\tau-1)]^{1/2}$. Equation (20) is easily solved by noting that the presence of the surface does not destroy translational invariance in the two directions parallel to the surface. If $\vec{x}_\parallel$ denotes the component of $\vec{x}$ in the plane parallel to the surface, then $s(x;l)$ is a function only of the combination $\vec{x}_\parallel - \vec{l}_\parallel$. Thus we write

$$s(\vec{x};\vec{l}) = \int\frac{d^2Q_\parallel}{(2\pi)^2}\,s_{Q_\parallel}(z,l_z)\,e^{i\vec{Q}_\parallel\cdot(\vec{x}_\parallel-\vec{l}_\parallel)}\,.$$

One easily obtains an equation for $s_{Q_\parallel}(z,l_z)$ along with the associated boundary condition. The solution is simply expressed in terms of the two quantities

$$\gamma(\vec{Q}_\parallel) = \xi^{-1}[1+(Q_\parallel\xi)^2]^{1/2}$$

and

$$\Gamma(\vec{Q}_\parallel) = 1 - \frac{2a_0\gamma}{1+4\Delta+a_0\gamma}\,.$$

We find

$$s_{\vec{Q}_\parallel}(z,l_z) = \frac{a_0}{2\gamma}\times\begin{cases}(1-\Gamma e^{-2\gamma l_z})\,e^{-\gamma(z-l_z)}, & z > l_z \quad (22a)\\ e^{+\gamma(z-l_z)} - \Gamma e^{-2\gamma l_z}e^{-\gamma(z-l_z)}, & 0<z<l_z\,. \quad (22b)\end{cases}$$

To compute the static correlation functions defined in Eq. (17), one needs the order parameters $\eta_{A,B}(\vec{x},\vec{l})$ and not simply $s(\vec{x};\vec{l})$. However, $\eta_A(\vec{x};\vec{l})$ and $\eta_B(\vec{x};\vec{l})$ are related by the homogeneous Eq. (18b). Thus from $s(\vec{x};\vec{l})$ and Eq. (18b), one may determine both $\eta_A(\vec{x};\vec{l})$ and $\eta_B(\vec{x},\vec{l})$. We write

$$\eta_{A,B}(\vec{x},\vec{l}) = \int\frac{d^2Q_\parallel}{(2\pi)^2}\,e^{i\vec{Q}_\parallel\cdot(\vec{x}_\parallel-\vec{l}_\parallel)}\,\eta_{A,B}(\vec{Q}_\parallel;z,l_z)\,,$$

and we find

$$\eta_A(\vec{Q}_\parallel;zl_z) = +(\tau/2)\,s_{\vec{Q}_\parallel}(z,l_z)\,, \tag{23a}$$

$$\eta_B(\vec{Q}_\parallel;zl_z) = -(1-\tau/2)\,s_{\vec{Q}_\parallel}(z,l_z)\,. \tag{23b}$$

The results exhibited in Eqs. (22) and (23) along with the definition of the Fourier transforms allow one to obtain the form of the static correlation functions defined in Eq. (17). Since the form of the Fourier transform is quite complex for general values of $\vec{l}$ and $\vec{l}'$, we consider two special cases. We also indicate how, in these special limits, the static correlation functions are related to be neutron and LEED cross sections for magnetic scattering above the Néel temperature.

(i) Suppose $\vec{l}$ and $\vec{l}'$ are both well inside the bulk of the material. Then the terms in Eqs. (22) proportional to $e^{-2\gamma l_z}$ may be ignored. This approximation is valid provided both l_z and l'_z refer to sites that lie a distance much greater than the correlation length ξ from the surface. In this limit, Eqs. (22) reduce to simply

$$s_{\vec{Q}_\parallel}(z,l_z) = (a_0/2\gamma)\,e^{-\gamma|z-l_z|}\,.$$

This result may be placed in a more conventional form by taking the Fourier transform with respect to z. Let

$$s_{\vec{Q}_\parallel}(z, l_z) = \int \frac{dQ_z}{2\pi} e^{iQ_z(z - l_z)} s(\vec{Q}).$$

A short calculation gives

$$s(\vec{Q}) = \frac{a_0}{\gamma^2 + Q_z^2} = \frac{a_0 \xi^2}{1 + (Q\xi)^2} ,$$

where $Q^2 = Q_\parallel^2 + Q_z^2$. Noting that $\xi^2 = a_0^2/6(T - T_N)$, one has

$$s(\vec{Q}) = \frac{a_0^3}{6(T - T_N)} \frac{1}{1 + (Q\xi)^2} . \tag{24}$$

From Eq. (24) one sees that the static correlation functions for the semi-infinite crystal reduce to the well-known Ornstein-Zernicke form when $\vec{l}$ and $\vec{l}'$ both lie a distance greater than the correlation length ξ from the surface.

The differential cross section per unit solid angle, $d\sigma/d\Omega$, for the scattering of neutrons from the bulk crystal is proportional to the quantity

$$S(\vec{q}) = \sum_{\vec{l}} e^{i\vec{q}\cdot(\vec{l} - \vec{l}')} \langle S_z(\vec{l}') S_z(\vec{l}) \rangle . \tag{25}$$

When the correlation functions derived from Eq. (24) are inserted into Eq. (25), one finds the Bragg intensity for the scattering of neutrons in directions close to the directions associated with antiferromagnetic Bragg scattering below T_N is proportional to $s(\vec{Q})$, where $\vec{q} = \vec{G} + \vec{Q}$ and $\vec{G}$ is a reciprocal-lattice vector of the antiferromagnetic crystal. Thus, as T_N is approached from above, one observes very strong critical scattering for wave-vector transfers $\vec{q}$ near $\vec{G}$ since $s(\vec{Q} = 0)$ diverges as $T \to T_N$ from above. Furthermore, the scattering intensity is confined to a smaller and smaller solid angle around the Bragg direction as T_N is approached from above, since the correlation length ξ becomes infinite as $T \to T_N$. This is the well-known magnetic critical scattering that one observes in neutron experiments as the temperature is lowered toward the Néel temperature.

(ii) We next consider the case where $l_z = 0$. Suppose that one of the two sites is situated in the crystal surface itself. We shall let site $\vec{l}$ lie in the surface by taking the limit $l_z \to 0$ in Eq. (22). Then, for $z > 0$, one has

$$s_{\vec{Q}_\parallel}(z, 0) = \frac{a_0}{2\gamma} (1 - \Gamma) e^{-\gamma z} = \frac{a_0^2 e^{-\gamma z}}{1 + 4\Delta + a_0\gamma} .$$

This result may also be written

$$s_{\vec{Q}_\parallel}(z, 0) = \frac{a_0^2 e^{-\gamma(Q_\parallel) z}}{1 + 4\Delta + \sqrt{6}\,(T - T_N)^{1/2} (1 + Q_\parallel^2 \xi^2)^{1/2}} . \tag{26}$$

Consider the nature of the static correlations between two spins situated within the surface layer. From Eq. (17) and Eq. (23), when τ is near unity one has

$$\langle S_z^{A,B}(l_\parallel', 0) S_z^A(l_\parallel, 0) \rangle = \pm \frac{S^2}{2} \int \frac{d^2 Q_\parallel}{(2\pi)^2} e^{iQ_\parallel \cdot (l_\parallel - l_\parallel')} s_{\vec{Q}_\parallel}(0, 0) \tag{27a}$$

$$= \pm \frac{a_0^2 S^2}{2} \int \frac{d^2 Q_\parallel}{(2\pi)^2} \frac{e^{iQ_\parallel \cdot (l_\parallel - l_\parallel')}}{1 + 4\Delta + \sqrt{6}\,(T - T_N)^{1/2} (1 + Q_\parallel^2 \xi^2)^{1/2}} . \tag{27b}$$

The plus sign is chosen for $\langle S_z^A(l_\parallel', 0) S_z^A(l_\parallel, 0) \rangle$, and the minus sign for $\langle S_z^B(l_\parallel', 0) S_z^A(l_\parallel, 0) \rangle$.

The function $s_{Q_\parallel}(0, 0)$ which forms the integrand of Eq. (27) differs from the function $s(\vec{Q})$ [Eq. (24)] examined earlier in the discussion of spin correlations in the bulk of the crystal in two very important ways. First of all, as we have seen, as $T \to T_N$ the function $s(\vec{Q})$ in Eq. (24) becomes singular at $\vec{Q} = 0$. In contrast to this, $s_{\vec{Q}_\parallel}(0, 0)$ remains finite at $\vec{Q}_\parallel = 0$, even when $T = T_N$. Second, we have seen that $s(\vec{Q})$ becomes more and more sharply peaked as a function of $\vec{Q}$ when T_N is approached from above. Even at $T = T_N$ the function $s_{\vec{Q}_\parallel}(0, 0)$ remains very broad, with no tendency to peak up at $\vec{Q}_\parallel = 0$ when T_N is approached from above. This last point may be appreciated by examining the form of $s_{\vec{Q}_\parallel}$ when $T = T_N$. One has

$$\lim_{T \to T_N} s_{Q_\parallel}(0, 0) = \frac{a_0^2}{1 + 4\Delta + a_0 |\vec{Q}_\parallel|} . \tag{28}$$

Thus, considered as a function of $\vec{Q}_\parallel$, $s_{\vec{Q}_\parallel}(0, 0)$ falls to half-maximum when $Q_\parallel = a_0^{-1}(1 + 4\Delta)$. Hence, the correlation length associated with the static correlation functions $\langle S_z^{A,B}(l_\parallel', 0) S_z(l_\parallel, 0) \rangle$ is always the order of a lattice constant, even at the Néel temperature.

If one considers low-energy electron scattering from the crystal and the incident beam interacts only with the surface layer, then the differential cross section per unit solid angle is proportional to[4]

$$s(\vec{q}_\parallel) = \sum_{l_\parallel} e^{i\vec{q}_\parallel \cdot (l_\parallel - l_\parallel')} \langle S_z(l_\parallel', 0) S_z(l_\parallel, 0) \rangle .$$

The function $s(\vec{q}_\parallel)$ is readily related to $s_{\vec{Q}_\parallel}(0, 0)$. If $\vec{q}_\parallel = \vec{G}_\parallel + \vec{Q}_\parallel$, where $\vec{Q}_\parallel$ is a reciprocal-lattice vector associated with the antiferromagnetic order in the surface layer, then we have

$$s(q_\parallel) = s_{\vec{Q}_\parallel}(0, 0) . \tag{29}$$

Equation (29), considered in the light of the remarks concerning the properties of the function $s_{\vec{Q}_\parallel}(0, 0)$ near T_N, implies that there should be no magnetic critical scattering of low-energy electrons from the crystal surface, as the Néel temperature is approached from above. The magnetic scattering

should be distributed over a large solid angle for T above T_N, with no pronounced narrowing in the angular distribution, or strong enhancement in magnitude as the temperature approaches T_N from above.

Palmberg and collaborators[2] have measured the temperature dependence of the LEED intensity for Bragg scattering from the surface NiO below T_N, as we have seen. These authors offer no comments on whether or not critical scattering above T_N is present.

More detailed studies of the magnetic scattering near the Néel temperature should provide an extremely useful means of probing the nature of spin correlations near the surface. It would be particularly interesting to investigate the occurrence of critical scattering as a function of incident-beam energy. When the electrons penetrate into the crystal a distance large compared to ξ, they should sample the spin fluctuations in the bulk, and critical scattering will result when the diffracted beam emerges near a direction associated with antiferromagnetic Bragg scattering from the bulk. Thus the study of the dependence of the critical scattering as a function of incident-electron energy provides, in principle, a means of probing the spatial variation of the critical spin fluctuations near the surface.

IV. LANDAU-GINZBURG THEORY OF SIMPLE CUBIC FERROMAGNET

It is straightforward to derive the Landau-Ginsburg equation and the boundary condition appropriate to the semi-infinite ferromagnet by the technique described in Sec. II. For the simple cubic ferromagnetic with a free (100) surface, the Landau-Ginsburg equation and the boundary condition have a form identical to Eqs. (7) and (8), provided an inhomogeneous term is added to the right-hand side of Eq. (7) if an external field is present. For a ferromagnet, the order parameter is

$$\eta(\vec{l}) = \langle S^z(\vec{l})\rangle / S \ .$$

Then, upon carrying out the procedure of Sec. II, we find for $\tau = T/T_C$ near unity,

$$(a_0^2/6)\nabla^2\eta(\vec{x}) + (1-\tau)\eta(\vec{x}) - \beta\eta^3(\vec{x}) = \tfrac{1}{3}(S+1)h(\vec{x}) \ , \tag{30}$$

where $h(\vec{x})$ is the externally applied field. The boundary condition is again

$$(1+4\Delta)\eta(x)\,\big|_{z=0} = a_0 \frac{\partial\eta}{\partial z}\bigg|_{z=0} , \tag{31}$$

where $\Delta = -\Delta J/J$ is a parameter that measures the amount by which the exchange between spins in the surface layer differs from the bulk value. As above, Δ is positive if the exchange in the surface is less than in the bulk.

Upon comparing Eqs. (30) and (31) with Eqs. (7) and (8), one sees that the magnetization in the surface of the semi-infinite ferromagnet is also described by the result exhibited in Eq. (16) for the geometry considered here.

Also, the static spin correlation function $\langle S_z(\vec{l}')S_z(l)\rangle$ has precisely the same form as the correlation function $\langle S_z^A(\vec{l}')S_z^A(\vec{l})\rangle$ for the semi-infinite antiferromagnet. Thus the discussion in Sec. III concerning the behavior of $\langle S_z^A(\vec{l}')S_z^A(\vec{l})\rangle$ for the antiferromagnet may be applied to the ferromagnet without alteration. Just as in the case of the semi-infinite antiferromagnet, there should be no magnetic critical scattering of low-energy electrons from the surface of the ferromagnet as the Curie temperature is approached from above, provided the energy of the incident electrons is sufficiently low that the penetration depth of the electron beam is small compared to the correlation length ξ.

It is interesting to examine the response of the semi-infinite ferromagnet to a uniform applied field. Suppose $T > T_C$, and let $h(\vec{x}) = h_0$, independent of x in Eq. (30). Then the η^3 term may be neglected if only the linear response of the medium is of interest. Furthermore, if the surface is in the x-y plane, $\eta(\vec{x})$ will depend only on z. In this circumstance, we find

$$\eta(z) = \frac{(S+1)h_0T_C}{3(T-T_C)} \times\left[1 - e^{-z/\xi}\left(\frac{1+4\Delta}{1+4\Delta+\sqrt{6}\,[(T-T_C)/T_C]^{1/2}}\right)\right] . \tag{32}$$

Far from the surface, where z is large compared to the correlation length ξ,

$$\eta(z) = \eta_\infty = \tfrac{1}{3}(S+1)\,[T_C/(T-T_C)]h_0 \ . \tag{33}$$

From Eq. (33) one obtains the Curie-Weiss law for the susceptibility of the extended ferromagnetic crystal.

In the surface layer the response of the spins to the external field is much weaker than the response of the spins in the bulk, when the temperature is close to the Curie temperature. From Eq. (32), one finds

$$\eta(0) = \left(\frac{2}{3}\right)^{1/2} \times \frac{(S+1)\,T_C^{1/2}h_0}{(T-T_C)^{1/2}\{1+4\Delta+\sqrt{6}\,[(T-T_C)/T_C]^{1/2}\}} \ . \tag{34}$$

From Eq. (34), one sees that the magnetization induced in the surface layer is smaller than that in the bulk by a factor of $(T-T_C)^{1/2}$, for T near T_C. A result of this form has been derived earlier[4]

from a microscopic theory of the semi-infinite ferromagnet, for the case $\Delta = 0$.

Notice that if the surface is stiffened sufficiently so that $1 + 4\Delta < 0$, then the denominator of Eq. (34) becomes singular at a temperature $T_C^{(s)} > T_C$. The molecular-field theory thus predicts that if the exchange in the surface is stronger than in the bulk, magnetic ordering in the surface region will occur in the temperature range $T_C < T < T_C^{(s)}$. For the reasons discussed in Sec. III such a true phase transition localized in the near vicinity of the surface will most likely not occur in a real crystal, although it is possible for the correlation length appropriate to the static correlation function $\langle S_z(\vec{l})S_z(\vec{l}')\rangle$ to become long compared to a lattice constant in this situation.

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Modified Potassium Dihydrogen Phosphate Model in a Staggered Field*

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The exact solution of the modified potassium dihydrogen phosphate model of a ferroelectric, previously considered in a direct field only, is now extended to include a staggered field. The thermodynamic properties are found to remain unchanged with the addition of a staggered field; namely, the specific heat vanishes below the transition temperature T_c and diverges as $(T - T_c)^{-1/2}$ above T_c. Phase diagrams similar to those of an antiferroelectric in a direct field are obtained. Behavior of the polarizations in both direct and staggered fields is also discussed.

I. INTRODUCTION

Considerable progress has been made in recent years in solving a number of two-dimensional ferroelectric models.[1] However, a few related problems still remain unsolved. One of the outstanding unsolved problems is the consideration of a staggered electric field. The staggered field is one which reverses direction from site to site thus playing the role of a direct field for an antiferroelectric. The staggered field is important to consider because it is the staggered polarization, for example, which is analogous to the spontaneous magnetization in a ferromagnet.[2] Unfortunately, the method of solution, namely the use of the Bethe ansatz, which proves to be useful in solving the previous ferroelectric models, is no longer applicable when a staggered field is present. A new approach is obviously needed to attack this problem.

We wish to report in this paper that there exists one model which is soluble by the existing method even when a staggered field is present. This is the modified potassium dihydrogen phosphate (KDP) model of a ferroelectric considered by the present author.[3,4] The modified KDP model is a special case of the general ferroelectric model and is unique in that its solution can be obtained independently by the method of Pfaffians. There is considerable interest in studying the behavior of a ferro-type model with a staggered field. In the magnetic language, e.g., this is equivalent to considering an antiferro-type model in a direct field. While the modified KDP model lacks the inversion symmetry with respect to the horizontal and vertical fields, it is quite symmetric as far as the staggered field is considered. Therefore the behavior of the modified KDP model with respect to the staggered field is typical of that of a ferroelectric model. This motivates our study since the Slater KDP model with a staggered field has not been solved. It turns out that the solubility of a ferroelectric model by the Pfaffian method is unaffected by the introduction of external, direct and staggered fields. Thus from the observation by the present author[5] that the par-