

# Model of the magnetic phase transition in a monolayer of molecules chemisorbed on the surface of a nonmagnetic metal

V. D. Borman, L. A. Maksimov, A. P. Popov, and V. I. Troyan

*Moscow Engineering-Physics Institute*

(Submitted 20 February 1981; resubmitted 3 April 1981)

Zh. Eksp. Teor. Fiz. **81**, 719–728 (August 1981)

A modified version of the Kittel model of antiferromagnetism is proposed for the description of the magnetic phase transition occurring in a monolayer of molecules chemisorbed on the surface of a nonmagnetic metal. This modification consists in the consideration of the dependence of the magnetic moments of the sublattices on the particle concentration and temperature. The model satisfactorily accounts for the available experimental data.

PACS numbers: 75.40. — s

## 1. INTRODUCTION

A magnetic phase transition (MPT) was recently detected with the aid of the thermomagnetic effect in a two-dimensional layer of carbon-monoxide molecules chemisorbed on the surface of platinum or gold, as well as of hydrogen molecules on the surface of platinum.<sup>1,2</sup> The MPT was observed as an abrupt change in the heat flux in a Knudsen gas at some value of the magnetic field.<sup>1,2</sup>

The surface MPT occurs in weak magnetic fields  $h_{ec} \sim 10^3$  Oe and at fairly high temperatures  $T \approx 300$  K, so that  $\mu_B h_{ec}/T \sim 10^{-4} \ll 1$  ( $\mu_B$  is the Bohr magneton). The value of  $h_{ec}$  does not change when the direction of the magnetic field relative to the surface is changed. The temperature dependence of the field is investigated in Ref. 2. It is shown that  $dh_{ec}/dT < 0$  and  $d^2h_{ec}/dT^2 \geq 0$  irrespective of the substrate and the adsorbate. The quantity  $h_{ec}$  increases with increasing molecule concentration on the surface. The width of the jump  $\Delta h$  does not exceed the error in the measurement of the intensity  $h$  of the magnetic field, i. e.,  $\Delta h/h_{ec} < 5 \times 10^{-2}$ .

It is natural to explain the observed surface MPT within the framework of models that admit of a discontinuous change in the properties at some magnetic-field value that does not depend on the direction of the field. This property is possessed by two well-known models of antiferromagnetism (AF): the Kittel model<sup>3</sup> and the biquadratic exchange model.<sup>4</sup> Let us note that allowance for the direct kinetic exchange in a system of molecules chemisorbed on a surface reveals the possibility under certain conditions of antiferromagnetic ordering in the chemisorbed layer.<sup>5,6</sup>

In the present paper we shall not discuss the question of the stability of long-range order in the two-dimensional system, since the weak logarithmic divergence due to the fluctuations can be eliminated by taking into consideration either the finiteness of the sample, or the weak interactions of the spin-orbit type.<sup>7</sup> The well-known proof of the impossibility of long-range order for a number of two-dimensional models<sup>7</sup> apparently does not extend to our case, since the chemisorbed layer is located on the surface of a solid. Furthermore, in the experiment the MPT was observed at  $h \neq 0$ , which, in

principle, can lead to long-range order in the two-dimensional system.

We shall use the Kittel model to describe the experimental data. It can be shown that the biquadratic-exchange model yields similar results. In the Kittel model the dependence of the sign of the interaction-exchange integral on strain results in a jump in the magnetic moment. The main experimental fact—the abrupt change in the properties of the surface in a weak field ( $\mu_B h_{ec} \ll T$ )—can be explained if we assume that the system is divided into aggregates that interact weakly with each other, but within each of which the interaction is strong. Then the weak magnetic field  $h_{ec}$  destroys only the mutual spin orientation of the aggregates, while the Curie temperature is determined by the strong interaction inside them. The weakness of the field  $h_{ec}$  should thus be related with the MPT in the macrosystem. Below as such aggregates we shall take two sublattices with a strong ferromagnetic (FM) interaction  $I_+$  within each sublattice and a weak antiferromagnetic (AF) interaction  $I_-$  between them.

The division of a quasi-two-dimensional system of molecules chemisorbed on the surface of a solid into two sublattices corresponds with the modern ideas about the chemisorption of simple gases on metals where two bond states  $\beta_1$  and  $\beta_2$  of the adsorbate are realized.<sup>8</sup> In a gradual deposition of the monolayer the bond state  $\beta_2$  is fixed until the degree of coverage of the surface  $\theta \sim 0.5$ , after which the deposition of the surface occurs in the  $\beta_1$  state. The particles are then deposited at the interstices of the “network” formed on the surface by the molecules in the  $\beta_2$  state.<sup>8</sup>

To account for the experimental data, we should modify the Kittel model. Thus, since the critical field depends on temperature and the concentration of molecules on the surface, we should take into account the dependence of the magnetic moments of the sublattices on temperature, and consider the case of different sublattice-occupation numbers. To take the indicated dependences into account correctly in the model expression for the free energy  $F$ , we shall use Kittel's form of the Hamiltonian and molecular field theory.

On the other hand, it is known that molecular field theory yields satisfactory results in the case of a large number of effectively interacting neighboring atoms. This generally explains why molecular field theory is not used to analyze two-dimensional systems, in which the number of such neighbors is small. But in the model under consideration here we shall consider not only the interaction with the nearest neighbors, but also the interaction with the next nearest neighbors, which is of the order of  $T$ .

We shall not discuss the role of the fluctuations in the phase transition under consideration. But we shall relate the observed MPT not to the attainment of a state of absolute instability, but to an equilibrium first-order phase transition in which the free energies of the various phases are equal. In the present paper we obtain from a comparison of the free energies of the noncollinear (NC) ferrimagnetic (FIM), and FM phases an expression for the critical field as a function of temperature and the concentration of molecules on the surface.

The modified Kittel model in question qualitatively accounts for all the available experimental data. Furthermore, it can be used to describe first-order phase transitions in three-dimensional magnetic bodies.

## 2. THE MODEL

Let us, in accordance with the foregoing, divide the quasi-two-dimensional system of molecules chemisorbed on a substrate into two sublattices 1 and 2. Let us denote by  $N$  the number of vacant sites in each of the sublattices, and by  $n_i$  the number of particles in the  $i$ -th sublattice. Let us introduce the concentrations  $c_i = n_i/N$ ,  $0 \leq c_i \leq 1$ . Below we shall assume that the particles in the sublattice 1 are in the  $\beta_1$  state, while those in the sublattice 2 are in the  $\beta_2$  state.

Let us write the Hamiltonian of the system in the form

$$H = -\frac{1}{2} \sum_{f,g} I(f-g) S_f S_g - h \sum_i S_i + N\kappa (I_- - I_c)^2. \quad (1)$$

The first term in (1) is the usual Heisenberg part of the isotropic spin-spin interaction Hamiltonian, the second term describes the interaction of the magnetic moments of the system with the magnetic field  $h$ , and the third term takes account of the dependence of the exchange integral on strain.  $I(f-g)$  is the integral for the exchange interaction between the magnetic moments  $S_f$  and  $S_g$  located at the sites  $f$  and  $g$ :  $I(f-g) = I_-$  if the sites  $f$  and  $g$  are nearest neighbors from different sublattices;  $I(f-g) = I_{+i}$  if the sites  $f$  and  $g$  are nearest neighbors in the  $i$ -th sublattice;  $\kappa$  and  $I_c$  are constants, with  $\kappa > 0$  and  $I_{+i} \gg |I_-| \sim |I_c|$ .

We obtain within the framework of molecular field theory the following expression for the free energy divided by  $N$ :

$$F = \frac{1}{2} I_{+i} c_i^2 \sigma_i^2 + \frac{1}{2} I_{+2} c_2^2 \sigma_2^2 + I_- c_1 c_2 \sigma_1 \sigma_2(k_1, k_2) - c_1 T \ln \frac{\text{sh}[B_1(S+1/2)/T]}{\text{sh}(B_1/2T)} - c_2 T \ln \frac{\text{sh}[B_2(S+1/2)/T]}{\text{sh}(B_2/2T)} + \kappa (I_- - I_c)^2, \quad (2)$$

where  $\sigma_i k_i$  is the mean value of the magnetic-moment vector of an occupied site in the  $i$ -th sublattice,  $|k_i| = 1$ ,  $S$  is the value of  $\sigma_i$  at  $T=0$ , and  $B_i$  is the magnitude of the molecular field in the  $i$ -th sublattice.

The molecular-field vector at the site  $f$  is given by the expression

$$B_f = h + \sum_g I(f-g) \sigma_g k_g, \quad (3)$$

where  $\sigma_g k_g$  is the mean value of the magnetic-moment vector of the occupied site  $g$ . Let us denote by  $m_i = c_i \sigma_i k_i$  the mean value of the magnetic-moment vector of a site in the  $i$ -th sublattice; then in our case of two sublattices we can write

$$B_1 = h + I_{+1} m_1 k_1 + I_- m_2 k_2, \quad (4)$$

$$B_2 = h + I_{+2} m_2 k_2 + I_- m_1 k_1.$$

Investigating the system of equations (4), we obtain for the FM state the expression

$$B_i = h + I_{+i} m_i + I_- m_i. \quad (5)$$

For the FIM state we obtain

$$B_i = |h + (-1)^i (I_{+i} m_i - I_- m_i)|. \quad (6)$$

If, on the other hand,  $k_1$  and  $k_2$  are disposed noncollinearly then for the NC state in the  $h \neq 0$  case we have the relation

$$B_i = (I_{+i} - I_-) m_i, \quad I_- (m_1 + m_2) = -h. \quad (7)$$

We have, in accordance with (2), (7), (5), and (6), three free energies corresponding to the NC, FM, and FIM states. The NC state is realized only when  $h \neq 0$ .

Our problem is to determine the law of magnetization of the system in question and the conditions under which the magnetic moment undergoes an abrupt change in some field  $h$ . In this connection, it is necessary to determine which of the three enumerated phases is realized at a given value of the magnetic field, and when one phase is replaced by another.

In accordance with (2) and (4), the quantities  $\sigma_1$  and  $\sigma_2$  satisfy the relations

$$\sigma_i = (S+1/2) \text{cth} [B_i(S+1/2)/T]^{-1/2} \text{cth} (B_i/2T). \quad (8)$$

Below we shall neglect in the expression (8) the quantities  $I_-$  and  $h$  in comparison with  $I_{+i}$ . Then  $\sigma_i$  is determined by the constant  $I_{+i}$  and by the temperature  $T$ , while the relations (8) are the equations determining the  $\sigma_i$ . This approximation is equivalent to the assumption that the  $\sigma_i$  are independent of the magnitude of the magnetic field.

It can be shown that if the concentration  $c_i$  does not depend on temperature, then as  $T$  is raised from zero to the Curie temperature,  $T_C^{(i)} = 1/3I_{+i} c_i S(S+1)$ , of the  $i$ -th sublattice,  $\sigma_i$  decreases monotonically from  $S$  to zero, the law of decrease being

$$\sigma_i \sim (T_C^{(i)} - T)^{1/2} \quad \text{for} \quad T \rightarrow T_C^{(i)} - 0. \quad (9)$$

Allowance for the dependence of the concentration on temperature leads to the decrease of the Curie temperature ( $dc_i/dT \leq 0$ ) in comparison with the case in which

$dc_i/dT=0$ . The quantity  $T_c^{(4)}$  is then determined from the equation

$$1/3 I_{+} c_i(T) S(S+1) = T. \quad (10)$$

Let us expand the spin part of the free energy  $F$  with allowance for (4) into a linear series in  $I_-$  and  $h$  about the point  $I_- = 0$ ,  $h = 0$ . Using in the process the relation (7), we obtain the sought model expression for the free energy of the NC phase:

$$F_{NC} = F_0(T) + h^2/2I_- + I_-(m_1^2 + m_2^2)/2 + \chi(I_- - I_c)^2. \quad (11)$$

Here  $F_0(T)$  is that part of the free energy which depends only on temperature. The quantities  $I_-$  and  $h$  are connected by a relation that can be determined by using the condition for the minimum of the free energy (11) with respect to the parameter  $I_-$ :

$$h = -2I_- [\chi(I_- - I_c) + (m_1^2 + m_2^2)/4]^{1/2}. \quad (12)$$

It is convenient to interpret the formula (12) as a means of parameterizing the magnetic field  $h$  with the parameter  $I_-$ . When  $h = 0$  the quantity  $I_-$  assumes the value

$$(I_-)_0 = I_c - (m_1^2 + m_2^2)/4\chi. \quad (13)$$

The connection between the parameter  $I_-$  and the quantity  $k_1 \cdot k_2$  is given by the following relation:

$$I_- = I_c + m_1 m_2 k_1 k_2 / 2\chi. \quad (14)$$

We can, proceeding in much the same way within the framework of the same approximation, obtain the free energies of the FM and FIM phases in a field:

$$F_{FIM} = F_0(T) + I_- m_1 m_2 - m_1^2 m_2^2 / 4\chi - h(m_2 - m_1), \quad (15)$$

$$F_{FM} = F_0(T) - I_- m_1 m_2 - m_1^2 m_2^2 / 4\chi - h(m_1 + m_2). \quad (16)$$

For definiteness, we assumed in computing (15) that  $m_2 > m_1$ .

It can be shown that the following inequalities are fulfilled for  $T < T_c^4$ ,  $I_c \leq 0$ , and  $h = 0$ :

$$F_{NC} \leq F_{FIM} \leq F_{FM}. \quad (17)$$

If  $I_c \geq 0$ , then  $F_{FM} \leq F_{FIM}$  for any value of  $h$ . It follows formally from (17) that  $F_{NC}$  is the smallest free energy for the indicated values of the parameter  $I_c$ . But for  $h = 0$  the NC state corresponds to

$$k_1 k_2 = -(m_1^2 + m_2^2) / 2m_1 m_2 \leq -1, \quad (18)$$

which does not make sense. Therefore, the FIM state with the free energy given by the formula (15) is realized when  $h = 0$  and  $I_c < 0$ .

For  $h \neq 0$  we eliminate the magnetic field  $h$  from the relations (11), (15), and (16), using the formula (12), in which  $I_-$  has a straightforward meaning only for the NC state. Further, we consider the quantities

$$\Delta_1(I_-) = F_{NC} - F_{FIM}, \quad \Delta_2(I_-) = F_{NC} - F_{FM}. \quad (19)$$

The equations  $\Delta_1 = 0$  and  $\Delta_2 = 0$  can be solved analytically. This allows us to determine the value of the parameter  $I_-$  and, consequently, the intensity of the magnetic field  $h$  with the aid of the formula (12) when  $F_{NC} = F_{FIM}$  or  $F_{NC} = F_{FM}$ , i. e., to determine the equilibrium-phase-transition point (with respect to the field) at which one magnetic phase is replaced by another.

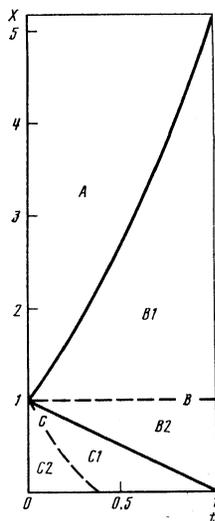


FIG. 1.

### 3. DISCUSSION OF THE RESULTS

The results of the analysis of the roots of the equations  $\Delta_1 = 0$  and  $\Delta_2 = 0$  and the corresponding magnetic field values given by (12), as well as the conditions under which the magnetic moment of the system changes discontinuously, can be illustrated as follows. Let us separate out in the plane  $t = m_1/m_2$ ,  $X = -2\chi I_c/m_2^2$  the semiinfinite strip  $X \geq 0$  and  $0 \leq t \leq 1$ , and divide it into three regions A, B, and C by the two lines  $X = t^2 + 3t + 1$  and  $X = 1 - t$  (see Fig. 1). Let us again divide the regions B and C by the lines  $X = 1$  and  $X = t^2 - 3t + 1$  each into two parts, as shown in Fig. 1. Thus, the region B consists of the parts B1 and B2; the region C, of the parts C1 and C2. The meaning of this division will become clear from the subsequent discussion.

It turned out that the law of magnetization, the types of phase transitions, and the possibility that the magnetic moment  $M = m_1 + m_2$  will undergo an abrupt change as the magnetic field  $h$  is increased depend on which

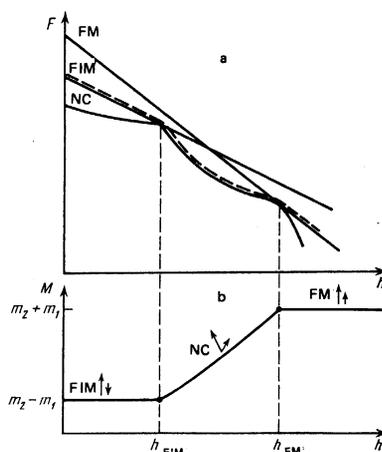


FIG. 2. Character of the dependence of (a) the free energies of the FM, FIM, and NC phases and (b) the magnetic moment of the system on the magnetic field for the region A.

of the regions *A*, *B* and *C* the point  $(t, X)$  belongs to. Therefore, let us consider each region separately, being interested in the equilibrium phase transition points.

**The region A.** As the field is increased, the initial FIM phase is replaced by the NC phase at the point  $h = h_{\text{FIM}}$  (see Fig. 2),

$$h_{\text{FIM}} = (-I_c + m_1 m_2 / 2\kappa) (m_2 - m_1), \quad (20)$$

through a second-order phase transition. The magnetic moment  $M = m_1 + m_2$  does not change at this point, but the susceptibility undergoes a jump. As  $h$  is increased further, the moment  $M$  increases smoothly from  $m_2 - m_1$  at the point  $h = h_{\text{FIM}}$  to  $m_1 + m_2$  at the point  $h = h_{\text{FM}}$  (see Fig. 2b), where

$$h_{\text{FM}} = (-I_c - m_1 m_2 / 2\kappa) (m_1 + m_2). \quad (21)$$

The NC phase is replaced by the FM phase, again through a second-order phase transition. Further increase of the field  $h$  does not change the magnetic moment of the system (Fig. 2b) within the framework of the approximation adopted above, as a result of which  $\sigma_i$  does not depend on  $h$ . Thus, if the point  $(t, X)$  is located in the region *A*, then both phase transitions are of second order, and a jump in the magnetic moment of the system is not realized.

**The region B.** As in the region *A*, the initial (at  $h = 0$ ) FIM phase is replaced by the NC phase at the point  $h = h_{\text{FIM}}$  through a second-order phase transition (see Fig. 3). As the field  $h$  is increased further, the moment  $M$  varies smoothly from  $m_2 - m_1$  at the point  $h = h_{\text{FIM}}$  to some critical value  $M_c < m_1 + m_2$  at the point  $h = h_c$ , where

$$h_c = \frac{1}{27\kappa} \left\{ [(m_1 + m_2)^2 - 6\kappa I_c - 3m_1 m_2]^{3/2} + (m_1 + m_2) \left[ (m_1 + m_2)^2 - 9\kappa I_c - \frac{9}{2} m_1 m_2 \right] \right\}. \quad (22)$$

Here a first-order phase transition occurs, the NC phase being replaced by the FM phase. In the process, the magnetic moment of the system changes discontinuously from the value  $M_c$  to  $m_1 + m_2$  (see Fig. 3b). The magnetic moment does not change when the field  $h$  is further increased.

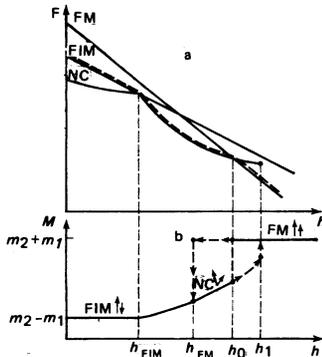


FIG. 3. Character of the dependence of (a) the free energies of the FM, FIM, and NC phases and (b) the magnetic moment of the system on the magnetic field for the region *B*. The arrows indicate the hysteresis loop for the region *B1*.

**The region C.** As the field  $h$  is increased, the FIM phase gets replaced by the FM phase at the point  $h = h_0$  (see Fig. 4), where

$$h_0 = -m_2 I_c, \quad (23)$$

through a first-order phase transition is accompanied by a discontinuous change of the magnetic moment of the system from  $m_2 - m_1$  to  $m_1 + m_2$  at the point  $h = h_0$ .

Thus, we arrive at the conclusion that a discontinuous change in the magnetic moment is realized in the system if the point  $(t, X)$  belongs to the region *B* or *C*. As can be seen from Fig. 3, if the point  $(t, X)$  is located in the region *B*, then the NC state, which, fieldwise, lies between the FIM and FM phases, is realized in the system when  $h \neq 0$ . If, on the other hand, the point  $(t, X)$  belongs to the region *C*, then the transition from the FIM phase into the FM phase occurs at one stroke.

It should be noted that the magnetization curves  $M(h)$ , which vary from region to region, match at the boundaries of the regions. The NC  $\rightarrow$  FM phase transition that then should occur at the boundary between the regions *A* and *B* is of third order, while the one that should occur at the boundary between the regions *B* and *C* is of first order.

Hysteresis phenomena are characteristic of first-order phase transitions. There exists some field range in which the NC phase for the regions *B* and *C1* (Figs. 3 and 4), or the FIM phase for the region *C* (Fig. 4), is metastable. No hysteresis phenomena occur in the region *A*. The metastability region for the NC or FIM phase is bounded from the right by the absolute-instability field  $h = h_{a11}$ . For the regions *B* and *C1*

$$h_{a11} = h_1 = \left(\frac{2}{3}\right)^{1/2} \frac{1}{2\kappa} \left(-2\kappa I_c + \frac{m_1^2 + m_2^2}{2}\right)^{3/2}. \quad (24)$$

For the region *C2* the field  $h_{a11}$  coincides with  $h_{\text{FM}}$ . The FM phase is metastable in a lower-field region. This region is bounded on the left by the absolute-instability field  $h_{a12} = h_{\text{FM}}$ . Notice that in region *B2*  $h_{\text{FM}} < h_{\text{FIM}}$ , and

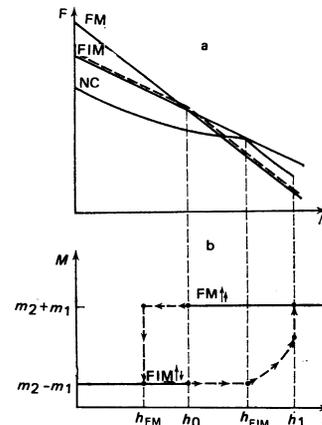


FIG. 4. Character of the dependence of (a) the free energies of the FM, FIM, and NC phases and (b) the magnetic moment of the system on the magnetic field for the region *C*. The arrows indicate the hysteresis loop for the region *C1*.

the inverse transition corresponding to the attainment of the state of absolute instability of the FM phase occurs straight into FIM phase. For  $X \leq t$ , we have, in accordance with (21),  $h_{FM} \leq 0$ .

Kittel's results<sup>3</sup> follow from the model (2) if we set  $m_1 = m_2 = S$  (this corresponds to the line  $t=1$  in Fig. 1). The FIM ( $k_1 k_2 = -1$ ) phase can, in contrast to the Kittel model, be also realized when  $h \neq 0$ .

Because of the fact that, during the experimental study of the MPT, the successively increasing magnetic-field values were periodically switched on and off,<sup>1,2</sup> the intensity of the critical field of the inverse transition is not known. The observed MPT can be related either to the equilibrium phase transition (at  $h = h_c$  or  $h_0$ ) or to the attainment of the state of absolute instability of the direct transition into the FM phase (at  $h = h_{ai1}$ ). In fact, the location of the transition point depends on the process of nucleation of the FM phase in the metastability region of the NC or FIM phase. Therefore, the observed MPT occurs in the field region bounded on the left by the critical field of the equilibrium phase transition and on the right by the field  $h_{ai1}$ . The slower this nucleation process is, the closer is the experimental value  $h_{ec}$  of the critical field of the transition to the field  $h_{ai1}$ . But since the temperature range (300–450 K) in which the MPT was experimentally investigated is fairly close to  $T_C \sim 500$  K, the observed MPT is apparently due to the attainment of the critical field of the equilibrium phase transition.

Let us recall that the experimental critical field  $h_{ec}$  of the jump increases with increasing concentration, and decreases with increasing temperature. It can be shown that the critical fields  $h_c$ (22),  $h_0$ (23), and  $h_1$ (24) increase when the concentrations  $c_1$  and  $c_2$  are increased wherever they have a meaning ( $h_c$  in the region B,  $h_1$  in the regions B and C2,  $h_0$  in the region C). We are, however, interested in the case in which, when the concentration is increased, only the quantity  $c_1$  increases, and  $c_2 = 1$ . As can be seen from the expression (23), the field  $h_0$  does not depend on the concentration  $c_1$  at all. The critical fields  $h_c$ (22) and  $h_1$ (24) increase with increasing  $c_1$ . It can also be verified that the fields  $h_c$  and  $h_1$  decrease with increasing temperature. It follows from the foregoing that the proposed model qualitatively describes the experimental dependences of the critical field  $h_{ec}$  of the jump on the concentration and temperature, and that the point  $(t, X)$  for the investigated system belongs to the region B.

As noted above, it was established in the experimental investigation of the MPT that

$$d^2 h_{ec} / dT^2 \geq 0. \quad (25)$$

Let us determine the conditions under which the fields  $h_c$  and  $h_1$  satisfy the relation (25). For this purpose, let us, for simplicity, see  $m_i = m(T)$  and  $c_i = 1$ . Let  $T \leq T_C$ ; then  $m \approx \gamma(T_C - T)^{1/2}$ . It can be verified that the relation  $d^2 h_i / dT^2 \geq 0$  is always satisfied in this approximation. For  $h_c$  the relation (25) is fulfilled in the vicinity of  $T_C$  provided

$$m^2(T) \geq -3(5^{1/2} - 1) \kappa I_c \quad (I_c < 0). \quad (26)$$

The condition for the existence of the magnetic-moment jump is then automatically fulfilled, since it has in this case ( $t=1$ ; see Fig. 1) the form

$$m^2(T) > -^2 / \kappa I_c. \quad (27)$$

The inequality (26) can be written in the form

$$T \leq T_C - \delta, \quad \delta = -27(5^{1/2} - 1) T_C \kappa I_c / 25 S^2 (S+1)^2. \quad (28)$$

From (27) we have the natural limitation on the quantity

$$-\kappa I_c < S^2 / 3(5^{1/2} - 1). \quad (29)$$

Then for  $\delta$  we shall have the following inequality:

$$\delta \leq T_C / 3(S+1)^2.$$

For  $S \sim 1$  and  $T_C \approx 500$  K the quantity  $\delta \sim 10$  K. For  $T > T_C - \delta$  the inequality  $d^2 h_c / dT^2 < 0$  will clearly be satisfied, and upon further increase of the temperature, the magnetic-moment jump will disappear and the transition into the FM state will be a second-order phase transition (the line  $t=1$  in the region A) when the inequality (27) is violated. Allowance for the  $c(T)$  dependence will evidently broaden the temperature range where the inequality (25) should be fulfilled.

Let the concentration  $c_2 = 1$ , and let the equilibrium concentration  $c_1 = c(T)$ . Let us also assume that  $I_{+1} < I_{+2} (T_C^{(1)} < T_C^{(2)})$ . Then, as the temperature  $T$  is raised, the point  $(t, X)$  (see Fig. 1), initially located in the region B, moves toward to the boundary between the B and A regions, or toward the boundary between the region B and C. In the first case the jump in the magnetic moment of the system decreases, vanishing at the boundary between the regions; the field also decreases, but remains finite at this boundary ( $h_c$  goes over into  $h_{FM}$ ). In the second case both the jump in the magnetic moment of the system and the field  $h_c$  remain finite at the boundary between the region B and C,  $h_c$  going over into  $h_0$ . As the temperature is raised further, the magnetic-moment jump decreases, and vanishes at  $t=0$ , but the field  $h_0$  does not depend on temperature on account of the assumption that  $I_c$ ,  $m_2 \approx \text{const}$ . The latter may be another reason why the relation (25) is fulfilled.

A similar picture obtains when the concentration  $c_1$  is decreased, except only that the critical field of the equilibrium phase transition into the FM states ceases to depend on the concentration when the point  $(t, X)$  reaches the boundary between the regions B and C, since the expression for  $h_0$  does not contain the quantity  $c_1$ .

It follows from the foregoing that, within the framework of the proposed model, the jump may vanish with  $h_c \neq 0$  upon further increase of the temperature or decrease of the equilibrium concentration.

When  $c_1$  is lower than some  $c_{cr}$  and  $c_2 \approx 1$ , we have a two-dimensional ferromagnet. As follows from the model under consideration, the jump in the magnetic moment of the system does not occur in this case when  $h$  is increased. Therefore, an experiment based on the thermomagnetic effect, and yielding a positive result only when  $h \neq 0$ , cannot identify the FM phase.

The thermomagnetic effect is an indirect method of investigating surface phase transitions. To get a complete idea about the phenomena occurring on the surface, we need to perform direct magnetic measurements.

Thus, the proposed model fully describes the qualitative experimental data reported in Ref. 2:

1) the model admits under certain conditions of an abrupt change in the magnetic moment of the system as the field intensity is increased;

2) because of the isotropy of the model, the intensity of the critical field of the jump does not depend on the direction of the magnetic field;

3) the expression for the critical field of the equilibrium phase transition does not explicitly contain the largest quantities of the problems ( $I_{*1}$ ,  $I_{*2}$ ,  $T$ ), and therefore the relation  $\mu_B h_c \ll T$  can be satisfied with fairly arbitrarily chosen values for the remaining parameters;

4) the critical field  $h_c$  increases as the particle concentration  $c_1$  on the surface increases;

5) the critical field  $h_c$  decreases with increasing temperature  $T$ ;

6) the expression for the field  $h_c$  satisfies under certain conditions the relation  $d^2 h_c / dT^2 \geq 0$ .

The proposed model allows us to predict the behavior of the system upon further increase of the temperature or decrease of the concentration. The width of the jump within the framework of the present treatment is equal to zero. The above-listed results [i.e., the results 1) - 6)] are also valid if the observed MPT is related with the attainment of a state of absolute instability.

In conclusion we thank É. L. Nagaev and his coworkers for an interesting discussion of the work at a seminar, as well as S. Yu. Davydov for useful comments.

<sup>1</sup>V. D. Borman, B. I. Buttsev, B. I. Nikolaev, and V. I. Troyan, *Zh. Eksp. Teor. Fiz.* **73**, 200 (1977) [*Sov. Phys. JETP* **46**, 103 (1977)].

<sup>2</sup>V. D. Borman, B. I. Buttsev, B. I. Nikolaev, A. P. Popov, and V. I. Troyan, *Zh. Eksp. Teor. Fiz.* **77**, 2297 (1979) [*Sov. Phys. JETP* **50**, 1105 (1979)].

<sup>3</sup>C. Kittel, *Phys. Rev.* **120**, 335 (1960).

<sup>4</sup>É. L. Nagaev, *Fizika magnitnykh poluprovodnikov* (The Physics of Magnetic Semiconductors), Nauka, Moscow, 1979, Chap. 2.

<sup>5</sup>S. Yu. Davydov, *Fiz. Tverd. Tela* (Leningrad) **20**, 1752 (1978) [*Sov. Phys. Solid State* **20**, 1013 (1978)].

<sup>6</sup>S. Yu. Davydov, A. P. Popov, and V. I. Troyan, *Fiz. Met. Metalloved.* **51**, 25 (1981).

<sup>7</sup>N. D. Mermin, *J. Phys. Soc. Jpn.* **26** (Suppl.), 203 (1969).

<sup>8</sup>Yu. K. Ustinov, Preprint Fiziko-Tekh. Inst. im A. F. Ioffe, No. 636, 1979.

Translated by A. K. Agyei