Kinetic theory of nonequilibrium processes on the surface of a magnet near its Curie point

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A kinetic theory is developed to describe nonequilibrium processes for particles with spin on the surface of a magnet in conditions of critical slowing down. A quasiclassical kinetic equation is obtained for the distribution function of the particles, and the effect of the magnetic interaction between the solid and the particle on the probability of escape of the particle from its potential well is determined. The experimentally observed anomalies in the temperature dependences of the rate of growth of the oxide film, the sublimation rate, and the desorption rate in the vicinity of the Curie point of the magnet are explained, and it is shown that they are principally due to singular behavior of the frequency of the particle relaxation associated with its coupling with the spin system of the solid.

1. INTRODUCTION

In the study of a number of phenomena occurring near the Curie (Néel) point T_K of a magnet, such as the sublimation of Co (Refs. 1, 2), the desorption of hydrogen from the surface of Ni (Ref. 3), the initial growth of oxide films on Fe (Ref. 4) and Co (Ref. 5), and the reduction of a nickel-oxide film on the surface of Ni (Ref. 6), it has been discovered that their rates K cannot be described by the Arrhenius law [$K = K_0 \exp(-E_a/T)$, where K_0 is a pre-exponential factor that depends weakly on the temperature T, and E_a is the activation energy]. Such anomalies in the dependence of $\ln K$ on $1/T$ have been exhibited by the presence of a cuspidal point at $T = T_K$, by the existence of a minimum in the paramagnetic region, and by a difference in the activation energies on opposite sides of the phase-transition point (for an illustration, see Fig. 2).

In the theory of processes (such as sublimation, desorption, and oxidation) characterized by a transition of a particle from one stable electronic state to another, the random-walk model is usually used (see, e.g., Refs. 7 and 8). Here we have in mind the emergence of a particle from a potential well under the influence of random forces due to fluctuations of the thermostat. The attempts undertaken earlier in Refs. 9 and 10 to explain the anomalies under consideration within the framework of a random-walk theory have not led to the creation of a model giving an adequate description of the experimental data.[1-6] All that was established was the possibility of a change of the activation energy upon passage through T_K for a particle possessing a magnetic moment.

The above anomalies of the temperature dependence of the rate were explained successfully for the first time in Ref. 11 for the example of the initial growth of an oxide film on Fe (Ref. 4). Features of nonequilibrium phenomena on the surface in the vicinity of the transition point of a bulk magnetic phase transition have been described successfully on the basis of the fluctuation theory of phase transitions and with the use of the phenomenological Fokker-Planck equation in the Kramers weak-friction approximation.[7]

In the present paper the theory is constructed and a physical mechanism of the observed phenomena is proposed.

Because of the exchange interaction of the particles under consideration with the surrounding atoms of the magnet, they are drawn into the collective fluctuations of the spin subsystem of the magnet. On the other hand, the escape of particles from the potential well, which determines the rate of the nonequilibrium processes under consideration, is due to the action of random forces associated with fluctuations of the magnet. Thus, the problem under consideration reduces to the simultaneous description of the dynamics of the fluctuations of the spin subsystem of the magnet and the nonequilibrium process of the escape of a particle from the well.

Below, in Sec. 2, for the pertinent hierarchy of characteristic times of the problem ($\tau_a \ll \tau_{sp} < \tau_r$, where τ_a is the period of the motion of the particle in the potential well, τ_{sp} is the relaxation time of the spin subsystem of the magnet, and τ_r is the energy-relaxation time of the particles), a kinetic equation is obtained for the quasiclassical distribution function of the particles in the case when they are not interacting with each other. In the derivation we start from the Liouville equation for the density matrix of the particle-magnet system and confine ourselves to the approximation quadratic in the interaction of the particle with the solid. As a result of coarsening performed over the time scale τ_{sp}, which includes, by virtue of the inequality $\tau_a \ll \tau_{sp}$, averaging over the rapid motion of the particle in the potential well, an equation is obtained for the energy distribution function of the particles in a three-dimensional potential well. The role of the potential field in which the particle moves is played by the free energy of the particle-solid system, which depends on the coordinate of the particle. The relaxation frequency $\omega \equiv \tau_r^{-1}$ appearing in the equation (the frequency of the relaxation of the energy distribution of the particles) is expressed in terms of the dynamical correlator of the random forces exerted by the solid on the particle. With this averaging the fast variables of the particle are eliminated from the analysis, and, in the case of slow relaxation of the energy distribution of the particles (when $\tau_r > \tau_{sp}$), the spin subsystem can be described with allowance for the order-parameter fluctuations, which relax over a time τ_{sp}. The resulting system of kinetic equations makes it possible to consider the process of the escape of the particle from the potential well as a consequence of fluctuations in the magnet

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near its T_K, if characteristic time t of this process satisfies the inequality $t > \tau_r > \tau_{sp}$.

The expression for the probability k of emergence of the particle from the potential well is obtained in Sec. 3. Of fundamental importance for the explanation of the anomaly in the vicinity of T_K is the linear dependence that the quantity k is found to have on the relaxation frequency ω, and also the mainly exponential dependence of the potential barrier on Q. In accordance with Ref. 12, for a time $t > \tau_r > \tau_{sp}$ the relaxation of the magnet near T_K is described by the critical-dynamics equation for the order parameter in the Gaussian approximation. The temperature dependence of the frequency of relaxation of the particle in its coupling with the spin subsystem of the magnet is calculated (see Sec. 4) for two critical-dynamics models with nonconserved energy that adequately model the experiment. It is found that in the model of the magnet with nonconserved spin the frequency $\omega \sim |\Delta T|^{-1/2}$ (where $\Delta T = T - T_K$), while in the model with conserved spin the frequency $\omega \sim |\Delta T|^{-3/2}$. Thus, for both critical-dynamics models the relaxation frequency ω increases as $T \to T_K$. The quantity Q (in the Gaussian approximation) does not have near T_K a singular part that is due to fluctuations of the spin subsystem (see Sec. 4).

In Sec.5 the theory developed is compared with experiment. As an example we consider the kinetics of the initial growth of an oxide film on metals. It is shown that the resulting temperature dependences of the particle-escape probability described within the experimental-error bars the experimental data on the initial oxidation of Fe (Ref. 4) and Co (Ref. 5). The region of applicability of the theory developed is discussed, and the temperature interval near T_K in which the theory ceases to apply is indicated.

2. THE KINETIC EQUATION

In the description of anomalies of nonequilibrium phenomena in the vicinity of T_K the fundamental question of the applicability of the well known theory of random walks arises. The basic kinetic equation in this theory (the Fokker–Planck equation) has been obtained previously[13] for particles with a large mass M ($M \gg m$, where m is the mass of an atom of the solid), when the characteristic time of the motion of the particle is much longer than the relaxation time (τ_s) of the solid and, by virtue of this, the solid can be regarded as a thermostat. We shall estimate the characteristic times of the problem. For a particle of mass $M \sim 10^{-22}$–10^{-23} g, moving in a potential well of depth $U \sim 1$ eV and characteristic size $a \sim 5$ Å, we have a period of motion of the order of $\tau_a \sim \pi a (2M/U)^{1/2} \sim 10^{-12}$–$10^{-13}$ sec. As the temperature approaches to within 2–3 K of T_K (as occurs in the experiments of Refs. 1–6) the relaxation time of the spin subsystem for Fe and Co does not exceed 10^{-9}–10^{-10} sec. Therefore, near T_K the opposite inequality $\tau_a \ll \tau_{sp} \sim \tau_s$ obtains. Over the time scale τ_a the spin subsystem does not reach equilibrium, and the use of the familiar random-walk model to describe the motion of the particle in the well is not justified. It becomes necessary to derive a kinetic equation for the case when the characteristic times have these relative magnitudes.

In deriving the kinetic equation we shall assume that the particles with spin that are situated on the surface of the magnet do not interact with each other. We shall start from the Liouville equation for the density matrix of the particle-solid system, which is describable by the Hamiltonian

$$\hat{H} = \hat{H}_0 + \frac{\hat{\mathbf{P}}^2}{2M} + \hat{\mathscr{V}}. \tag{2.1}$$

Here $\hat{H}_0$ describes the solid, $\hat{\mathbf{P}}^2/2M$ describes the translational motion of the particle, of mass M, and the operator $\hat{\mathscr{V}}$ is the energy of the interaction of the particle with the atoms of the solid, including their exchange interaction. Since in the derivation of the kinetic equation there is no need to single out the exchange interaction in explicit form in $\hat{\mathscr{V}}$, henceforth in Sec. 2, to simplify the expressions, we shall omit the spin operators of the particle and the magnet when listing the arguments of $\hat{\mathscr{V}}$. The motion of a particle of mass $M \sim 10^{-22}$ g at a temperature $T \sim 10^3$ K can be described in the quasiclassical approximation. In fact, with an interaction range $R_0 \sim 5$ Å we have $R_0 P \sim 10^{-25}$ erg·sec, and, therefore, $R_0 P \gg \hbar$.

We shall obtain the kinetic equation as follows. We perform a Wigner transformation of the Liouville equation, and then take the trace of the resulting equation over the variables of the solid. We next perform smoothing over the time scale τ_s, which amounts to averaging over the rapid motion of the particle and averaging over the distribution with respect to the internal degrees of freedom of the solid. The averaging over the rapid motion is necessary in the smoothing procedure in the case under consideration, since the characteristic time of the motion of the particle in the potential well is shorter than the relaxation time of the solid. We note that the averaging over τ_a and over τ_s is performed over different variables; therefore, for convenience in the mathematical calculations we shall average first over τ_s and then over τ_a. After performing the Wigner transformation and closing the kinetic equation for the particle distribution function $f(\mathbf{R},\mathbf{P},t)$, we obtain

$$\frac{\partial f}{\partial t} + \frac{\mathbf{P}}{M}\frac{\partial f}{\partial \mathbf{R}} + \langle \hat{\mathbf{F}} \rangle \frac{\partial f}{\partial \mathbf{P}} = J_{coll}\ . \tag{2.2}$$

By $\langle \ldots \rangle$ here we mean $\mathrm{Sp}(\rho_0 \ldots)$ [$\mathrm{Sp} \equiv \mathrm{Tr}$]. Since the relaxation times of the electron subsystem are $\tau_e \sim 10^{-15}$ sec, while those of the phonon subsystem are $\tau_{ph} \sim 10^{-11}$ sec, and these are much shorter than τ_{sp}, in the Gaussian approximation used below (noninteracting electron, phonon, and spin subsystems) we shall mean by the density matrix in the absence of the particle (ρ_0) the product of the equilibrium density matrices of the electron and phonon subsystems and the density matrix of the spin subsystem, which depends on the order parameter $\sigma(r,t)$. In (2.2) the force acting on the particle is determined by the expression

$$\hat{\mathbf{F}} = -\partial \hat{V}/\partial \mathbf{R}, \tag{2.3}$$

where

$$\hat{V} \equiv \hat{V}(\mathbf{R}) = \langle \mathbf{R} | \hat{\mathscr{V}}(\hat{\mathbf{R}}) | \mathbf{R} \rangle.$$

In calculating the collision integral J_{coll} we have kept only the terms quadratic in the interaction of the particle with the solid:

$$J_{\text{coll}} \approx -\frac{\partial}{\partial \mathbf{P}} \mathrm{Sp}\left[\hat{\mathbf{F}} \int_0^\infty d\tau \exp\left(-\tau \frac{\mathbf{P}}{M} \frac{\partial}{\partial \mathbf{R}} \right) \hat{R}(-\tau) f(t-\tau) \right], \tag{2.4}$$

where

$$\hat{R}(-\tau) f(t-\tau) = -e^{-i\tau \hat{L}_0} \left(\frac{i}{\hbar} [\Delta \hat{V}, \rho_0] f(t-\tau) + \frac{1}{2} \{ \hat{\mathbf{W}}, \rho_0 \}_+ \frac{\partial f(t-\tau)}{\partial \mathbf{P}} \right), \tag{2.5}$$

$$\hat{L}_0 \hat{A} = \frac{1}{\hbar} [\hat{H}_0, \hat{A}]. \tag{2.6}$$

In (2.5) and below, $\Delta \hat{V} = \hat{V} - \langle \hat{V} \rangle$, and the operator $\hat{\mathbf{W}}$ of the random force denotes $\hat{\mathbf{F}} - \langle \hat{\mathbf{F}} \rangle$. We shall consider the collision integral in more detail. Since the estimate

$$\frac{P}{M} \frac{\partial}{\partial R} \sim \frac{1}{\tau_a}$$

is valid, the integral in (2.4), because of the operator $\exp[-\tau(\mathbf{P}/M)(\partial/\partial \mathbf{R})]$ in the integrand, accumulates most of its value over the time interval $[0, \tau_a]$. The distribution function of the particles changes appreciably only over a time interval of the order of τ_r. Consequently, taking the hierarchy of times $\tau_r > \tau_s \gg \tau_a$ into account, we can neglect the dependence on τ of the function $f(t-\tau)$:

$$f(t-\tau) \underset{\tau \ll \tau_r}{\longrightarrow} f(t). \tag{2.7}$$

The formula (2.7) implies neglect of nonlocality in time, or of memory effects, this being possible solely by virtue of the hierarchy of times in the problem. Neglecting in (2.4) terms of order $\hbar/RP$ and τ_a/τ_r, we can write Eq. (2.2) in the form

$$\frac{\partial f}{\partial t} + \frac{\mathbf{P}}{M} \frac{\partial f}{\partial \mathbf{R}} + \langle \hat{\mathbf{F}} \rangle \frac{\partial f}{\partial \mathbf{P}} - \mathbf{G} \frac{\partial f}{\partial \mathbf{P}} = \frac{\partial}{\partial P_i} \left(D_{ik} \frac{\partial f}{\partial P_k} \right) + \frac{\partial}{\partial P_i} (\omega_{ik} P_k f). \tag{2.8}$$

After the quasiclassical limit $\hbar \to 0$ is taken, the coefficients in (2.8) are determined by the formulas

$$D_{ik} = \frac{1}{2} \int_0^\infty d\tau \langle \{ \hat{W}_k, \hat{W}_i(\tau) \}_+ \rangle, \tag{2.9}$$

$$\omega_{ik} = \frac{1}{MT} \int_0^\infty d\tau \langle \hat{W}_k \hat{W}_i(\tau) \rangle, \tag{2.10}$$

$$\mathbf{G} = -\frac{1}{2T} \frac{\partial}{\partial \mathbf{R}} \langle (\Delta \hat{V})^2 \rangle. \tag{2.11}$$

As will be clear from Sec. 4, the expression $\langle \hat{\mathbf{F}} \rangle - \mathbf{G}$ can be represented as $-\partial F/\partial \mathbf{R}$, where F denotes the free energy of the particle-solid system. Here, in the expression for F the interaction of the particle with the solid should be taken into account as a perturbation to the free energy of the solid in the approximation quadratic in $\hat{V}$. Therefore, (2.4) is a Fokker–Planck equation in which the role of the potential is played by the free energy of the system.

Since $\tau_a < \tau_{\text{sp}}$, it is necessary to average Eq. (2.8) over the rapid motion of the particle in the well. For this it is convenient to go over to the coordinate system whose axes coincide with the principal axes of the tensors D_{ik} and ω_{ik}. In this system of coordinates, $D_{ik} = D_i \delta_{ik}$ and $\omega_{ik} = \omega_i \delta_{ik}$. Since $\tau_a \ll \tau_r$, it is reasonable to suppose that the oscillations of the particle in the well are weakly damped, so that it is sufficient to represent the average force $\langle \hat{\mathbf{F}} \rangle$ in the form of the first terms of its series in powers of $\mathbf{R}$:

$$\langle \hat{F}_i \rangle \approx -M\omega_{0i}^2 R_i + B_i R_i^2 + C_{ik} R_i R_k, \qquad i \neq k, \tag{2.12}$$

where B_i and C_{ik} are constants and ω_{0i} is the eigenfrequency of the ith vibrational mode of the particle. Representing $\langle \hat{\mathbf{F}} \rangle$ in the form (2.12) makes it possible to calculate the probability of emergence of the particle from the well. Following Ref. 14, in the phase space of the particle we go over, for each vibrational mode (ω_{0i}) of the particle, to a coordinate frame rotating together with the particle, in the clockwise direction, with frequency ω_{0i}. In this coordinate frame the particle is almost stationary (since the damping is small, and $\tau_a \ll \tau_r$). Next we average each term of Eq. (2.8) (with allowance for (2.12)) over a time $t \gg \tau_a$. In the averaging of the kinetic equation (2.12) with allowance for the random-phase hypothesis the terms $B_i R_i^2 (\partial f/\partial P_i)$, $C_{ik} R_i R_k (\partial f/\partial P_i)$, and $\mathbf{G}(\partial f/\partial \mathbf{P})$ vanish. Omitting the intermediate algebraic transformations, we finally obtain the equation for the distribution function depending on the energy of the particle

$$E = \sum_i E_i = \sum_i P_i^2/2M + \sum_i M\omega_{0i}^2 R_i^2/2,$$

in the form

$$\frac{\partial f(E,t)}{\partial t} = \sum_i \left[\omega_i \frac{\partial}{\partial E_i} (E_i f) + \frac{D_i}{M} \frac{\partial}{\partial E_i} \left(E_i \frac{\partial f}{\partial E_i} \right) \right]. \tag{2.13}$$

The quantity ω_i in (2.13) has the meaning of the relaxation frequency of the energy distribution of the particles, and D_i is the coefficient of diffusion of the particles in the phase space. It is straightforward to convince oneself that the quantities ω_i and D_i are related to each other: $D_i = M\omega_i T$. The expression for ω_i follows from the formula (2.10). Thus, as a result of the above averaging over the fast motion of the particle and over the distribution of the solid, over a time scale τ_s, for the energy distribution function of the particles we obtain a kinetic equation in which the collision integral coincides with the collision integral of the Fokker-Planck equation.

3. PROBABILITY OF EMERGENCE OF THE PARTICLE FROM THE POTENTIAL WELL

The probability k of emergence of the particle from the well is determined by a ratio of moments of the distribution function—the ratio of the flux w_B of particles leaving the well to the number n_A of particles in the well.

To calculate k we shall assume that the depth Q_i of the well for each of the three modes ($i = 1,2,3$) is sufficiently large so that $Q_i \gg T$. In this case the flux w_B is obviously small and can be assumed to be stationary; in this case the quantity n_A can also be assumed to be constant. The flux w_B

will be stationary only if $\partial f/\partial t = 0$. The kinetic equation (2.13) reduces to an equation of the form

$$\sum_i \frac{\partial}{\partial E_i}\left\{\omega_i E_i\left(f+T\frac{\partial f}{\partial E_i}\right)\right\}=0. \tag{3.1}$$

In the case of one mode, Eq. (3.1) coincides in form with the stationary equation for the distribution function of particles executing one-dimensional motion in a deep potential well in the Kramers weak-friction approximation,[7] i..e., when $\tau_s \ll \tau_a \ll \omega^{-1}$. Using (3.1), we can obtain an expression for the probability of emergence of the particle from the well:

$$k=\omega\frac{Q}{T}e^{-Q/T}. \tag{3.2}$$

In (3.2) the quantity Q is defined in terms of the free energy of the particle-magnet system at the points A (F_A) and B(F_B) (see Fig. 1):

$$Q=F_B-F_A. \tag{3.3}$$

The expression (3.2) determines the probability of emergence of the particle from the well for one particular mode. Similar expressions for the escape probability are also obtained for the other two modes. It is obvious that the largest contribution to the total escape probability is given by the probability of escape across the lowest barrier. Neglecting, on this basis, the contribution from the escape across the other barriers, we find that the probability of emergence of the particle from the potential well in the case of three-dimensional displacement is determined approximately by the formula (3.2). We note that the expression (3.2) for the particle-escape probability is the same both in the case under consideration near the Curie point, when $\tau_a \ll \tau_s < \tau_r$, and far from T_K, i.e., is the same independently of the relative magnitudes of τ_a and τ_s.

It is clear from what has been said above that to determine the temperature dependence of the probability of emergence of the particle from the potential well in conditions of critical slowing down of the magnet we must calculate the relaxation frequency ω of the particle and the magnitude Q of the potential barrier with allowance for the exchange interaction between the particle and the solid.

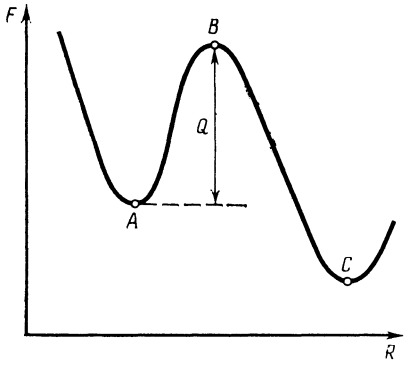

FIG. 1.

4. THE PARTICLE-RELAXATION FREQUENCY AND POTENTIAL BARRIER

The Hamiltonian $\hat{H}_0$ of the solid and the interaction potential $\hat{\mathscr{V}}$ can be represented in the form

$$\hat{H}_0=\hat{H}_{\text{e-ph}}+\hat{H}_{\text{sp}}, \tag{4.1}$$

$$\hat{\mathscr{V}}=\hat{\mathscr{V}}_{\text{e-ph}}+\hat{\mathscr{V}}_m, \tag{4.2}$$

where $\hat{H}_{\text{e-ph}}$ describes the electron and phonon subsystems of the solid, $\hat{H}_{\text{sp}}$ is the spin subsystem of the solid, and $\hat{\mathscr{V}}_{\text{e-ph}}$ and $\hat{\mathscr{V}}_m$ are the energies of interaction of the particle with the electron and phonon subsystems and with the spin subsystem of the magnet, respectively. Taking (4.1) and (4.2) into account, we can write the free energy F of the particle-magnet system in the form

$$F=F_{\text{e-ph}}+F_m+\frac{\mathbf{P}^2}{2M}. \tag{4.3}$$

In (4.3) $F_{\text{e-ph}}$ denotes the free energy of the electron and phonon subsystems of the solid with allowance for their interaction with the particle, and F_m is the free energy of the spin subsystem with allowance for the exchange interaction of the magnet with the particle. The neglect of the interaction between the spin subsystem and the electron and phonon subsystems implies that the analysis is limited to taking fluctuations into account in the Gaussian approximation. Therefore, even when the exchange interaction of the particle with the magnet is taken into account as a perturbation to the free energy F_0 of the spin subsystem of the magnet, it is sufficient to confine ourselves to the term quadratic in the interaction and to write F_m in the form

$$F_m=F_0+\langle\hat{V}_m\rangle-\frac{1}{2T}\langle(\hat{V}_m-\langle\hat{V}_m\rangle)^2\rangle, \tag{4.4}$$

$$\hat{V}_m=\langle\mathbf{R}|\hat{\mathscr{V}}_m|\mathbf{R}\rangle. \tag{4.5}$$

The operator $\hat{\mathscr{V}}_m$ is determined by the set of spin operators of the magnet and by the operator $\hat{\mathbf{S}}$ of the particle spin, and depends on the particle coordinate $\mathbf{R}$.

Near T_K the spin subsystem of the magnet can be described by a classical ordering field,[15] or, equivalently, one can use a block model of the magnet.[12] In this case the expression for the free energy of the spin subsystem can be written in the Landau-Ginzburg form:

$$F_0/T=\int_\Omega d\mathbf{r}[a_2\sigma^2+a_4\sigma^4+c(\nabla\sigma)^2], \tag{4.6}$$

where $\boldsymbol{\sigma}(\mathbf{r},t)$ (the order parameter) is the vector field of the spin of the block with center at the point $\mathbf{r}$. In (4.6) $a_2=a_2'(T-T_K)$, with $a_2'>0$, and a_4 and c are smooth functions of the temperature ($a_4>0$); Ω denotes the volume of the solid. In the expression (4.5) we can go over from the set of spin operators to $\boldsymbol{\sigma}(\mathbf{r},t)$ and represent the magnetic interaction $\hat{V}_m$ between the solid and a particle with spin on its surface in a spin-polarized state[16,17] in the form

$$\hat{V}_m=\int_\Omega d\mathbf{r}\,J(|\mathbf{R}-\mathbf{r}|)\,\hat{s}\sigma(\mathbf{r},t), \tag{4.7}$$

where $J(|\mathbf{R}-\mathbf{r}|)$ is the exchange integral, which is a rapidly

decreasing function of the distance between the particle and the block. The expression (4.7) makes it possible to take into account the main factor in the problem under consideration—the effect of fluctuations of the magnetic moment of the solid on the motion of a particle with spin interacting with it. From (4.7) it is clear that, by virtue of the symmetry of the problem, $\hat{V}_m$ can depend only on the coordinate Z of the particle along the normal: $\hat{V}_m = \hat{V}_m(Z)$.

We turn to the calculation of the contribution of the magnetic interaction of the particle with the solid to the relaxation frequency of the particle. In accordance with the formulas (2.3) and (4.2) it can be seen that the random force is equal to the sum of the random forces exerted on the particle by the electron and phonon subsystems and by the spin subsystem of the magnet. Then, using the independence of the averaging over the subsystems of the magnet, we find, in accordance with the formula (2.6), that the relaxation frequency can be separated into two terms:

$$\omega_i(\omega_i)_{\text{e-ph}} + (\omega_i)_m, \tag{4.8}$$

where $(\omega_i)_{\text{e-ph}}$ and $(\omega_i)_m$ are the relaxation frequencies of the particle in its coupling with the electron-phonon subsystem and the spin subsystem, respectively, of the solid. Since in the model under consideration the magnetic interaction depends only on the coordinate Z of the particle ($\hat{V}_m = \hat{V}_m(Z)$) it follows from the formula (2.10) that only $(\omega_z)_m$ is nonzero. It is not difficult to convince oneself that only $(\omega_z)_{\text{e-ph}}$ makes a contribution to the expression (3.2) for the probability of emergence of the particle from the well. Below, therefore, we shall calculate ω_z:

$$\omega_z \equiv \omega = \omega_{\text{e-ph}} + \omega_m. \tag{4.9}$$

In a small neighborhood of T_K the quantity $\omega_{\text{e-ph}}$ can be assumed to be independent of temperature. We shall determine the dependence of ω_m on the temperature. In accordance with (2.3), (2.10), and (4.7), ω_m can be represented in the form

$$\omega_m = \frac{S(S+1)}{MT}\int_0^\infty d\tau \int_{-\infty}^{\infty} \frac{d\mathbf{k}}{(2\pi)^3} G(\mathbf{k},\tau)\int_\Omega d\mathbf{r}\frac{\partial J(|\mathbf{R}-\mathbf{r}|)}{\partial Z} \times e^{i\mathbf{kr}}\int_\Omega d\mathbf{r}'\frac{\partial J(|\mathbf{R}-\mathbf{r}'|)}{\partial Z}e^{-i\mathbf{kr}'}. \tag{4.10}$$

In (4.10) the dynamic correlation function $G(\mathbf{k},\tau)$ is defined by the formula

$$G(\mathbf{k},\tau) = \langle(\sigma_{\mathbf{k}}(0) - \langle\sigma_{\mathbf{k}}(0)\rangle)(\sigma_{\mathbf{k}}^*(\tau) - \langle\sigma_{\mathbf{k}}^*(\tau)\rangle)\rangle, \tag{4.11}$$

where $\sigma_{\mathbf{k}}(t)$ is the Fourier transform of $\sigma(\mathbf{r},t)$:

$$\sigma_{\mathbf{k}}(t) = \Omega^{-1/2}\int_\Omega d\mathbf{r}\, e^{-i\mathbf{kr}}\sigma(\mathbf{r},t). \tag{4.12}$$

We shall make use of a critical-dynamics model to determine the function $\sigma_{\mathbf{k}}(t)$. Since in the experiments of Refs. 1–6 the temperature of the magnet was held constant, two critical-dynamics models with nonconserved energy of the magnet are adequate. For these models $\sigma_{\mathbf{k}}(t)$ satisfies the equation[12]

$$\frac{\partial\sigma_{\mathbf{k}}(t)}{\partial t} = -\gamma_0\frac{\delta(F/T)}{\delta\sigma_{\mathbf{k}}^*} + \zeta_{\mathbf{k}}(t), \tag{4.13}$$

where the function $\zeta_{\mathbf{k}}(t)$ describes the random influences exerted on the $\mathbf{k}$th mode of the order parameter by all the other degrees of freedom of the magnet. The model with nonconserved spin has $\gamma_0 = \text{const}$, while the model with conserved spin has $\gamma_0 = \varepsilon\mathbf{k}^2$ (ε is a constant).

Equation (4.13) is substantially different for $\mathbf{k} = 0$ and for $\mathbf{k}\neq 0$. However, to calculate ω_m from the formulas (4.10) and (4.11) there is no need to solve Eq. (4.13) for $\mathbf{k} = 0$, since the value of the definite integral (over $\mathbf{k}$) is not changed when the integrand is changed at a finite number of points.

We shall consider the case $\mathbf{k}\neq 0$. Using (4.3), (4.4), and (4.6), and the uniformity of the average value $\langle\sigma\rangle$ (Ref. 18), we obtain

$$\frac{\delta(F/T)}{\delta\sigma_{\mathbf{k}}^*} = \frac{\delta(F_0/T)}{\delta\sigma_{\mathbf{k}}^*}, \qquad \mathbf{k}\neq 0. \tag{4.14}$$

In accordance with Ref. 15, the expression for F_0/T (in the Gaussian approximation) has the form

$$F_0/T = \begin{cases} \sum_{\mathbf{k}} (a_2 + c\mathbf{k}^2)|\sigma_{\mathbf{k}}|^2, & T>T_K, \\ -\frac{a_4}{\Omega}\sigma_0^4 + \sum_{\mathbf{k}}(2a_2 + c\mathbf{k}^2)|\sigma_{\mathbf{k}}|^2, & T<T_K. \end{cases} \tag{4.15}$$

On the basis of (4.14) and (4.15), Eq. (4.13) can be written in the form

$$\frac{\partial\sigma_{\mathbf{k}}}{\partial t} = -\frac{\gamma_0}{2G(\mathbf{k},0)}\sigma_{\mathbf{k}} + \zeta_{\mathbf{k}}(t), \qquad \mathbf{k}\neq 0, \tag{4.16}$$

where the static correlator $G(\mathbf{k},0)$ is determined by the expressions

$$G(\mathbf{k},0) = \tilde{\xi}^2/2c(1+\mathbf{k}^2\tilde{\xi}^2), \tag{4.17}$$

$$\tilde{\xi} = \begin{cases} \xi, & T>T_K, \\ \xi/2^{1/2}, & T<T_K, \end{cases} \qquad \xi = (c/a_2'|T-T_K|)^{1/2}. \tag{4.18}$$

Using the solution of (4.16) and the equality $\langle\sigma_{\mathbf{k}}(0)\zeta_{\mathbf{k}}^*(t)\rangle = 0$, we obtain, in accordance with (4.11), an expression for $G(\mathbf{k},\tau)$:

$$G(\mathbf{k},\tau) = G(\mathbf{k},0)\exp[(-\gamma_0/2G(\mathbf{k},0))\tau], \quad \mathbf{k}\neq 0. \tag{4.19}$$

Substituting (4.19) into the expression (4.10) for ω_m, integrating over the time, and using the evenness of the function $G^2(\mathbf{k},0)/\gamma_0$, we obtain

$$\omega_M = \frac{2S(S+1)}{MT}\int_{-\infty}^{\infty}\frac{d\mathbf{k}}{(2\pi)^3}\frac{G^2(\mathbf{k},0)}{\gamma_0}\int_\Omega d\mathbf{r}\frac{\partial J(|\mathbf{R}-\mathbf{r}|)}{\partial Z} \times\int_\Omega d\mathbf{r}'\frac{\partial J(|\mathbf{R}-\mathbf{r}'|)}{\partial Z}\cos[\mathbf{k}(\mathbf{r}-\mathbf{r}')]. \tag{4.20}$$

We shall assume that $J(|\mathbf{R}-\mathbf{r}|)$ can be represented in the form

$$J(|\mathbf{R}-\mathbf{r}|) = J\theta(r_0 - |\mathbf{R}-\mathbf{r}|). \tag{4.21}$$

Here J is a constant and $\theta(r_0 - |\mathbf{R} - \mathbf{r}|)$ is the Heaviside function. The representation of the exchange integral in the form (4.21) means that the particle interacts with the block spin if the distance between them does not exceed r_0. Integrating in (4.20) with allowance for (4.21) gives for the cases of nonconserved and conserved spin of the magnet, respectively,

$$\omega_m = \frac{\pi S(S+1) J^2 r_0^4 \theta(r_0-d)}{16\gamma_0 MT\{a_2' c^3[1+\theta(T_K-T)]\}^{1/2}} |\Delta T|^{-1/2}. \quad (4.22)$$

$$\omega_m = \frac{\pi S(S+1) J^2 r_0^4 \theta(r_0-d)}{16\varepsilon MT(a_2')^{3/2}[1+\theta(T_K-T)]^{3/2} c^{1/2}} |\Delta T|^{-3/2}. \quad (4.23)$$

In (4.22) and (4.23) the quantity d is the distance of the particle from the surface of the magnet. In accordance with (4.22) and (4.23), the relaxation frequency of the particle in its coupling with the spin subsystem of the magnet increases as T_K is approached. In accordance with (4.19) and (4.20), this is due to the increase of both the amplitude and the lifetime of the spin-density fluctuations.

We now calculate the contribution of the magnetic interaction to the magnitude of the potential barrier (3.3). For this we shall show first that the fluctuation term $\langle(\hat{V}_m - \langle\hat{V}_m\rangle)^2\rangle/2T$ in the expression (4.4) for the free energy does not give rise to singularities in the temperature dependence of the latter near T_K. Using (4.7), it is not difficult to convince oneself that

$$\langle(\hat{V}_m - \langle\hat{V}_m\rangle)^2\rangle = S(S+1)\int_{-\infty}^{\infty}\frac{d\mathbf{k}}{(2\pi)^3} \times G(\mathbf{k},0)\int_\Omega d\mathbf{r} J(|\mathbf{R}-\mathbf{r}|)e^{i\mathbf{kr}}\int_\Omega d\mathbf{r}' J(|\mathbf{R}-\mathbf{r}'|)e^{-i\mathbf{kr}'}. \quad (4.24)$$

Substituting (4.21) into (4.24) and integrating over $\mathbf{k}$, we obtain the estimate

$$\langle(\hat{V}_m - \langle\hat{V}_m\rangle)^2\rangle \sim 1/\xi \sim (|T_K - T|)^{1/2}. \quad (4.25)$$

It is clear from the expression (4.25) that fluctuations of the order parameter do not lead to divergence of F_m as $T \to T_K$. Since the fluctuation term has the same temperature dependence as $\langle\hat{V}_m\rangle$, and, moreover, is small in comparison with $\langle\hat{V}_m\rangle$, and since our aim is to describe anomalies in the dependence of $\ln k$ on $1/T$ near T_K, we can neglect the fluctuation term in the calculation of Q. Substituting (4.21) into (4.7) and taking it into account that, in the Gaussian approximation,[18]

$$\langle\sigma_{\mathbf{k}}\rangle = \left[\Omega\frac{a_2'}{2a_4}(T_K-T)\theta(T_K-T)\right]^{1/2}\delta_{\mathbf{k},0}$$

we have

$$\langle\hat{V}_m\rangle = \frac{2\pi}{3}JS(r_0^3-d^3)\theta(r_0-d)\left[\frac{a_2'}{2a_4}(T_K-T)\theta(T_K-T)\right]^{1/2}. \quad (4.26)$$

Using the result, we write on the basis of (3.3), (4.3), and (4.4) the expression for Q in the form

$$\frac{Q}{T} = \frac{Q_0}{T_K}x + \alpha[(x^2-x)\theta(x-1)]^{1/2}, \quad (4.27)$$

where

$$\alpha = \frac{2\pi}{3}JS(d_A^3 - d_B^3)(a_2'/2a_4T_K)^{1/2},$$

$x = T_K/T$, and $d_{A(B)}$ is the value of d in the case when the particle is at the point $\mathbf{R}_{A(B)}$. The quantity Q_0 is the potential barrier due to the interaction of the particle with the electron subsystem of the solid.

The formula (4.27) was obtained with the use of the inessential assumption that d_A and d_B are smaller than r_0. In a small neighborhood of T_K the quantity Q_0 can be assumed to be constant. We stress that the second term in the right-hand side of (4.27) describes the effect of the magnetic interaction of the particle with the solid and is nonzero only for $T < T_K$. The expressions (3.2), (4.9), (4.22), (4.23), and (4.27) make it possible to calculate the probabilities of escape of a particle from a potential well near T_K. From the formulas obtained it follows that far from T_K the dependence of $\ln k$ on T_K/T is linear, and the change of the slope is due to the switching on of the magnetic interaction between the particle and the solid as the temperature is lowered through T_K. The minimum in the paramagnetic region and the divergence at $T = T_K$ (in the dependence of $\ln k$ on T_K/T) are due to the anomalous increase of the relaxation frequency (ω_m) of the particles near the Curie point of the magnet. In conclusion, we stress that replacement of the dependence (4.21) of the exchange integral on the distance by another (e.g., exponential) dependence does not affect the character of the temperature dependences of ω_m and Q/T.

Thus, the picture that emerges of the influence of the dynamics of the fluctuations on the probability of escape of a particle from a potential well reduces to the following. The increase of the amplitude and lifetime of the fluctuations in the vicinity of T_K leads to an anomalous increase of the random force and to an increase of the time for which it acts on the particle spin. As a result, the relaxation frequency (determined by the correlator of the random forces) of the energy distribution of the particles increases as T_K is approached. On the other hand, for a particle with spin, because of the change of the contribution of the exchange interaction as the temperature passes through T_K, the magnitude of the potential barrier changes. The anomalies in the temperature dependence of the probability of escape of the particle from the potential well turn out to be related to both the change of the frequency of relaxation of the energy distribution of the particles and the change of the magnitude of the potential barrier.

5. COMPARISON OF THE THEORY WITH EXPERIMENT. DISCUSSION OF THE RESULTS

In the experiments of Refs. 4 and 5 the authors investigated the temperature dependence of the mass K of oxygen absorbed by unit area of the surface of a sample (Fe, Co) per unit time in the stage of growth of the oxide film in which the film is up to a few hundred angstroms thick. The dependence of $\ln K$ on $1/T$ far from T_K was observed to be linear, with different slopes of the straight-line segments below and above T_K, and it was also found that near T_K the dependence of $\ln K$ on $1/T$ has a minimum in the paramagnetic region and a cuspidal point at $T = T_K$ (see Fig. 2).

The rate of growth of a thin oxide layer is determined by the passage of ions of the metal through the metal–oxide

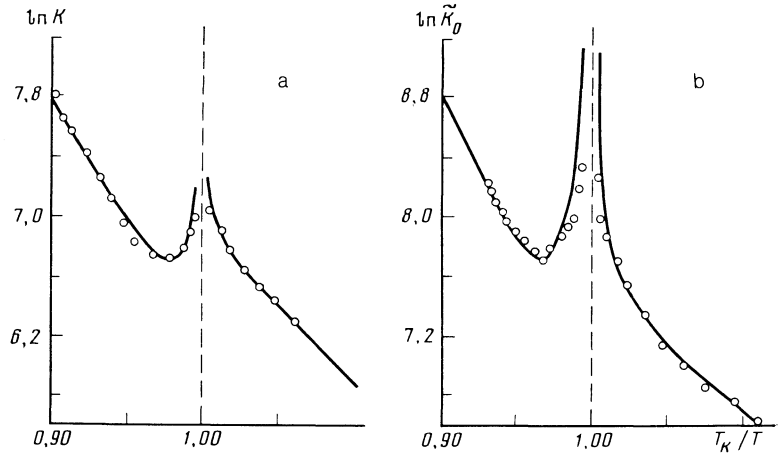

FIG. 2. Comparison of the theory with experiment: a) the points are experimental data for Fe from Ref. 4; the solid line is the theoretical dependence corresponding to formulas (3.2), (4.9), (4.22), and (4.27); the following parameter values are used: $Q_0/T_K = 25$, $\alpha = -9.2$, $A_0 = [\pi S(S+1)/16\gamma_0 \times Mc^2\omega_{\text{e-ph}} T_K]J^2 r_0^4 (c/a_2' T_K)^{1/2} = 1.5$; $[K] = \mu\text{g/cm}^2\cdot\text{sec}$; b) the points are experimental data from Ref. 5; $\tilde{K}_0 = K\tilde{\beta}$, $\tilde{\beta} = 14$ sec; the solid line is the theoretical dependence corresponding to the formulas (3.2), (4.9), (4.23), and (4.27); the following parameter values are used: $Q_0/T_K = 24$, $\alpha = -8.0$, $B_0 = [\pi \times S(S+1)/16\varepsilon Mc^2\omega_{\text{e-ph}} T_K J^2 r_0^4 (c/a_2' T_K)^{3/2} = 5\cdot 10^{-3}$.

interface,[19] and can depend, therefore, on the exchange interaction in the magnet. When comparing the theory with experiment (Figs. 2a and 2b) it is necessary to take into account that the quantity K is connected with the probability of emergence of a particle (metal ion) from a potential well by the relation

$$k = K/mN, \tag{5.1}$$

in which m is the mass of the oxygen atom and N is the number of oxygen atoms in the oxide per unit area of the surface of the sample. The relation (5.1) implies that an oxygen atom becomes bonded to one atom of the magnet, forming FeO or CoO, as is characteristic for the conditions of the experiments of Refs. 4 and 5.

Since the question of the applicability of the critical-dynamics models used to describe the magnetic phase transitions in Fe and Co is open, the experimental data have been compared with the dependences obtained for the models with conserved spin and with unconserved spin. It has been established that within the limits of the experimental error the data for Fe (Ref. 4) are described with the use of Eq. (4.22) (see Fig. 2a), while the data for Co (Ref. 5) are described with the use of Eq. (4.23) (see Fig. 2b). The parameter values found (see the captions to Figs. 2a and 2b) make it possible to estimate $\omega_{\text{e-ph}}$. For this we substitute the experimental value of K (with allowance for (5.1)), taken far from T_K, into the formulas (3.2), (4.9), (4.22) [or (4.23)], and (4.27). Far from T_K the contribution of ω_m to the relaxation frequency ω can be neglected, so that by setting $mN \sim 10^{-2}$ $\mu\text{g/cm}^2$ we obtain the value $\omega_{\text{e-ph}} \sim 10^9$ sec^{-1}. Thus, the inequality $\omega^{-1} > \tau_s$ of the relaxation times of the particle and solid, which was assumed to be valid in the solution of the problem, is fulfilled in the experiments under consideration. That the relaxation frequency of the particles is so small (in comparison with the characteristic frequency $\sim 10^{13}$ sec^{-1} of the intramolecular vibrations) is due, as shown in Ref. 20, to the slow modulation of the equilibrium position of the particle by the low-frequency vibrations of the lattice.

We shall estimate the region of applicability of the approach being developed. Representing the free energy F_0 in the form (4.6) is admissible for temperatures satisfying the inequality $|T - T_K| \ll T_K$ (Ref. 18). From this interval we must exclude a region from T_1 to T_2 including T_K, in which the theory is inapplicable for the following reasons. The kinetic description of the behavior of the particle, starting from which we have obtained all the results, is valid only in the case when the inequalities $\tau_a \ll \tau_s < \tau_r$ are fulfilled. The inequality $\tau_a \ll \tau_s$ for a particle in a deep well is always fulfilled, if only because of the phonon subsystem. The inequality $\tau_s < \tau_r$ is valid only in a certain range of temperatures, since in the vicinity of the Curie point τ_s is determined by τ_{sp}, which increases as T_K is approached, while the particle-relaxation time, equal to $\tau_r \equiv (\omega_{\text{e-ph}} + \omega_m)^{-1}$, decreases as a consequence of the increase of ω_m [see (4.22) or (4.23)]. Qualitatively, this situation is characterized by Fig. 3.

The temperature dependence of τ_{sp} can be easily estimated on the basis of simple arguments. The diffusion of the order parameter $\boldsymbol{\sigma}(r,t)$ is described by the equation[21]

$$\frac{\partial \boldsymbol{\sigma}}{\partial t} = D_0 \nabla^2 \boldsymbol{\sigma}. \tag{5.2}$$

The scale-invariance hypothesis[18] makes it possible to estimate the diffusion coefficient D_0 (Ref. 22):

$$D_0 \approx \frac{T_K}{\hbar} a_0^2 \left(\frac{T - T_K}{T_K}\right)^{\nu(1-\eta)/2} \tag{5.3}$$

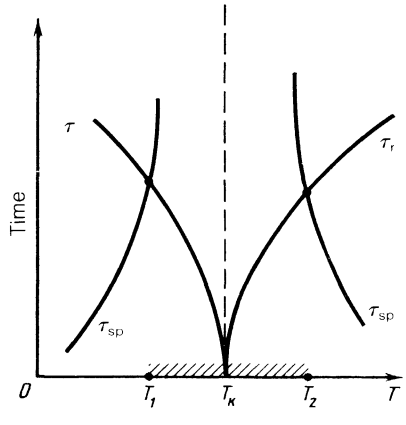

FIG. 3. In the temperature range from T_1 to T_2 the inequality $\tau_s < \tau_r$ is not fulfilled, and therefore the theory is inapplicable.

In formula (5.3) the quantity a_0 is of the order of the interatomic spacing, and ν and η are critical exponents. The relaxation of a perturbation in the spin subsystem at a specified temperature occurs in a time τ_{sp}, during which the perturbation of the spin density does not leave the region of equally oriented spins, i.e., a region with characteristic linear dimensions of the order of the correlation length ξ. In accordance with random-walk theory,

$$\xi^2 \approx D_0 \tau_{sp}. \tag{5.4}$$

The temperature dependence of ξ is determined by the exponent ν in the formula[15]

$$\xi = a_0 \left(\frac{T - T_K}{T_K} \right)^{-\nu}. \tag{5.5}$$

Using (5.3)–(5.5) we have

$$\tau_{sp} \approx \frac{\hbar}{T_K} \left(\frac{T_K}{T - T_K} \right)^{5/4}. \tag{5.6}$$

In the presently considered case of the Gaussian approximation we have $\nu = \frac{1}{2}$ and $\eta = 0$ (Ref. 15), and, in accordance with (5.6), τ_{sp} can be estimated as

$$\tau_{sp} \approx \frac{\hbar}{T_K} \left(\frac{T - T_K}{T_K} \right)^{-\nu(5+\eta)/2} \tag{5.7}$$

The formula (5.7) is in reasonable agreement with the experimental data of Ref. 23 on neutron scattering by iron. At temperature $T = T_K + 14.1$ K the half-width of the spectrum of the scattered neutrons is $\Gamma = 2.74 \cdot 10^{-5}$ eV. The relaxation time of the spin subsystem in this case is equal to $\tau_{sp} = \hbar/\Gamma = 2.4 \cdot 10^{-11}$ sec. According to the formula (5.7), for $T - T_K = 14$ K we have $\tau_{sp} \approx 3 \cdot 10^{-12}$ sec.

The temperature range from T_1 to T_2 (see Fig. 3) within which the inequality $\tau_{sp} < (\omega_{e\text{-}ph} + \omega_m)^{-1}$ is not fulfilled is determined using (5.7) and (4.22) or (4.23), and the values found for $\omega_{e\text{-}ph}$ for Fe and Co. From the analysis performed it follows that the theory can be used in both cases for temperatures differing from T_K by not less than 2 K. Thus, the inequality used between the characteristic times of the problem is fulfilled in the experiments for the entire temperature range investigated.

In conclusion, we shall make a few remarks. Apparently, the first attempt to explain the anomalies in the temperature dependence of the rate of oxidation of Fe in the initial stage[4] was made by Suhl.[9] The author assumed that it is sufficient to take into account only the fluctuational modulations of the potential barrier. From the result obtained above it is clear that with this approach it is possible to explain only the change of the activation energy as the temperature passes through T_K. And it was precisely such a result that was obtained by Suhl.

The expression (3.2) for the probability k of escape of the particle from the potential well coincides in form with the expression for the probability in the case $\tau_s \ll \tau_a \ll \tau_r$, obtained by Kramers[7] on the basis of the Fokker–Planck equation. Therefore, it can be said that in the present paper we have given, on the one hand, a justification of the Kramers expression used in Ref. 11 for the case of weak friction ($\tau_a \ll \tau_r$), and, on the other hand, an answer to the question posed by the authors of Ref. 24 concerning the incorrectness (because of memory effects) of the use of a Kramers expression for k near T_K.

The escape of the particle from the well can be regarded as a cooperative dynamical effect—on the one hand, the particle executes motion in the well, and, on the other hand, it participates in the collective oscillations of the spin subsystem of the magnet. The oscillations of the particle in the well occur on a nonequilibrium solid, since $\tau_a \ll \tau_{sp}$. A transition of the particle from one energy level to another, which occurs (in accordance with the theory described above) on account of fluctuations of the solid over a characteristic time $\tau_r > \tau_{sp}$, can be assumed to occur on an equilibrium magnet. Such a description becomes possible by virtue of the coarsening carried out over the time scale τ_s, by means of which the fast variables of the particle were eliminated. In this sense the above analysis confirms the idea, put forward in Ref. 11, that results obtained in the weak-friction approximation in random-walk theory are applicable to the description of the phenomena under consideration.

We note that the fact that a satisfactory description of the experimental data has been achieved in the framework of the Gaussian approximation is evidently due to the fact that the observed features of the temperature dependence of K are determined principally by the singularity of the frequency of relaxation of the particles near T_K. In accordance with formula (4.10) the term ω_m in the expression for the relaxation frequency of the particles is determined as an integral of a correlation function of the magnet. The behavior of the latter near the Curie point is determined by the critical exponent γ, whose value in the Gaussian approximation ($\gamma = 1$) differs from its experimental value $\gamma \approx 1.40$ (see Ref. 25). However, the integration leads to smoothing of the errors arising from the use of the Gaussian approximation. Thus, the theory developed in the Gaussian approximation is suitable for the description of the kinetics of the sublimation, desorption, and growth of a thin oxide film on a magnet, and of the reduction kinetics, in a range of temperatures sufficiently close to T_K.

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