The effect of thermal fluctuations on the FMR line shape in dispersed ferromagnets

Yu. L. Raikher and V. I. Stepanov

Institute of the Mechanics of Continuous Media, Ural Division of the Russian Academy of Sciences
(Submitted 5 May 1992)
Zh. Eksp. Teor. Fiz. **102**, 1409–1423 (October 1992)

We investigate magnetic resonance in a superparamagnet, and derive the dynamic susceptibility of an ensemble of randomly oriented single-domain anisotropic ferromagnetic particles. We show that as the temperature rises, the orientational fluctuations of the magnetic moment simultaneously weaken the inhomogeneous broadening of the FMR line arising from the distribution in the directions of anisotropy axes of the particles and create an even stronger homogeneous (superparamagnetic) broadening. A particular result of the combined action of these effects is the nonmonotonic temperature dependence of the FMR linewidth in dispersed ferromagnets, which is well known in experiments.

INTRODUCTION

Continuing interest in the study of the physical properties of ultradispersed ferromagnets and ferrites by ferromagnetic resonance (FMR) is fueled by the appearance of entirely new media belonging to this class: glasses and zeolites that incorporate transition metals,[1,2] magnetic liquids,[3] heterogeneous metal polymers,[4] biogenic magnetite,[5] etc. However, theoretical interpretation of the FMR spectra obtained remains a complicated problem.

In an ultradispersed ferromagnet, the characteristic size of a particle is 50 to 200 Å. Even taken by itself, the smallness of the particle size causes peculiarities in the magnetic behavior. First of all, it is well-known[6,7] that a ferromagnetic microcrystal with a volume $V\sim 10^{-18}$ cm^3 has no domain structure, i.e., it is uniformly magnetized and possesses a constant magnetic moment $\mu = M_s V$, where M_s is the magnetization of the material that makes up the particle. Secondly, for $V\sim 10^{-18}$ cm^3 and $M_s \sim 10^3$ G the random magnetic field induced by thermal fluctuations, whose amplitude H_f should equal $k_B T/\mu$ in order of magnitude, reaches room temperature values $H_f \geqslant 10^2$ Oe, and consequently becomes commensurate with the field H_a for the magnetic anisotropy of the material. It is this orientational diffusion of the vector $\boldsymbol{\mu}$ under the action of $\mathbf{H}_f$ that causes, among other things, the superparamagnetism of dispersed ferromagnets.

The theoretical study of FMR taking into account the superparamagnetic effects, is the subject of this paper. In Ref. 8, equations were obtained that describe the motion of the magnetic moment of a single-domain particle at finite temperatures, and the temperature and frequency dependences of the natural FMR parameters were studied for particles with the "easy axis" type of anisotropy. In Ref. 9, the dynamic susceptibility of an isotropic superparamagnet was calculated; in Refs. 10, 11, FMR was investigated in an anisotropic particle placed in a constant external field $H \gg H_a$.

It is this latter problem that is closest in its formulation to the situation encountered in experiment. Actually, the overwhelming majority of data published to date on FMR in dispersed ferromagnets (see, e.g., Refs. 1,2,4,10,12–15) were obtained from measurements in a magnetizing field H at a fixed resonant excitation frequency $\omega/2\pi \sim 10$ GHz, which corresponds to $H\sim 3\cdot 10^3$ Oe. Thus, the condition $H \gg H_a$ is fulfilled for any dispersed ferromagnet in which the anisotropy field is a few hundred oersteds.

The goal of this paper is to apply the theoretical results of Refs. 9 and 11 to FMR in solid dispersed ferromagnets. Calculating the dynamic susceptibility using these results requires averaging not only over the statistical ensemble of particles with a given direction of the anisotropy axis, but also over the orientational texture of the sample, i.e., over the angular distribution of the anisotropy axes in such a particle. In what follows, we show that this second stage of averaging changes the observed dynamic susceptibility in a nontrivial way, and in particular allows us to obtain a temperature and field dependence of the FMR parameters that is qualitatively close to what is observed in experiment. Specifically, the discussion will center around the following phenomena: an increase in asymmetry of the absorption line as the temperature drops, a decrease in the linewidth ΔH as T increases, and an increase or decrease of the resonant field H_{res} as the temperature changes, depending on the sign of the magnetic anisotropy constant of the dispersed particles.

1. DYNAMICS OF THE MAGNETIC MOMENT OF A SUPERPARAMAGNETIC PARTICLE

In investigating the motion of the magnetic moment $\boldsymbol{\mu}$ of a single-domain particle at temperatures that are nonzero but not too close to the Curie point, it is natural to assume $\mu = \mathbf{M}_s V = \text{const}$.

This allows us to study only the rotation of the magnetic moment, which we write in the form $\boldsymbol{\mu} = \mu \mathbf{e}$, where $\mathbf{e}^2 = 1$. In a statistical ensemble, the macroscopic (observed) magnetic moment of a particle should be defined as the average of the "microscopic" vector $\boldsymbol{\mu}$:

$$\langle \boldsymbol{\mu} \rangle = \mu \langle \mathbf{e} \rangle = \mu \int \mathbf{e} W(\mathbf{e}, t)\, d\mathbf{e}, \tag{1}$$

where $W(\mathbf{e},t)$ is an orientational distribution function which satisfies the kinetic equation[8]

$$\partial W/\partial t + (\hat{\mathbf{J}}(\boldsymbol{\Omega} W)) = 0. \tag{2}$$

Here, $\hat{\mathbf{J}} = [\mathbf{e}\nabla]$ is the infinitesimal rotation operator, and $\nabla = \partial/\partial \mathbf{e}$ is the gradient evaluated at the surface of the unit sphere. The angular velocity $\boldsymbol{\Omega}$ of the unit vector $\mathbf{e}$ is split up

 0038-5646/92/100764-08$05.00

into a regular (field-induced) and diffusive (fluctuation) part: $\boldsymbol{\Omega} = \boldsymbol{\Omega}_r + \boldsymbol{\Omega}_f$. The expression for the regular component follows from the Landau-Lifshitz equation[7]

$$\partial\boldsymbol{\mu}/\partial t = -\gamma[\boldsymbol{\mu}\mathbf{H}_r] - (\alpha\gamma/\mu)[\boldsymbol{\mu}[\boldsymbol{\mu}\mathbf{H}_r]], \tag{3}$$

where γ is the gyromagnetic ratio, α is the dimensionless relaxation time, and $\mathbf{H}_r = -\partial U/\partial\boldsymbol{\mu} = -(1/\mu)\nabla U$ is the magnetic field defined by the orientation-dependent portion $U(\mathbf{e})$ of the total energy of the particle. Writing (3) in the form of a kinematic relation $\dot{\mathbf{e}} = \boldsymbol{\Omega}_r\mathbf{e}$ and introducing the operator $\hat{\mathbf{P}} = \hat{\mathbf{J}} + (1/\alpha)\nabla$, we obtain

$$\boldsymbol{\Omega}_r = \gamma\mathbf{H}_r + \alpha\gamma[\mathbf{e}\mathbf{H}_r] = -(\alpha\gamma/\mu)\hat{\mathbf{P}}U. \tag{4}$$

We find the rate of random motion $\boldsymbol{\Omega}_f$ (see Ref. 8) by replacing the regular field $\mathbf{H}_r$ by the random field $\mathbf{H}_f = -(k_B T/\mu)\nabla\ln W$ in (4). From this the total rate of rotation of the magnetic moment is

$$\boldsymbol{\Omega} = -(\alpha\gamma/\mu)\hat{\mathbf{P}}(U + k_B T\nabla\ln W). \tag{5}$$

Substituting (5) into (1) leads to a kinetic equation in the form

$$2\tau\partial W/\partial t = (\hat{\mathbf{J}}W\hat{\mathbf{P}})(U/k_B T + \ln W), \tag{6}$$

where we introduce the notation $\tau = \mu/2\alpha\gamma k_B T$ for the characteristic orientational diffusion time of the magnetic moment.

Under steady-state conditions, for which the magnetic field is $H = \text{const}(t)$, the solution to Eq. (6) corresponding to equilibrium is a Gibbs distribution

$$W_0 = Z_0^{-1}\exp(-U_0/k_B T), \quad Z_0 = \int\exp(-U_0/k_B T)\,d\mathbf{e}, \tag{7}$$

with $U_0 = -\mu(\mathbf{eH})$. Switching on a variable field $\mathbf{h}(t)$ perturbs the thermodynamic equilibrium and causes the magnetic moment to move, which is described by the kinetic equation (6) with $U = U_0 - \mu(\mathbf{eh})$. The quantity of interest in magnetic resonance is the nonequilibrium portion of the macroscopic magnetic moment

$$\mathbf{m} = \mu(\langle\mathbf{e}\rangle - \langle\mathbf{e}\rangle_0). \tag{8}$$

Here angle brackets without labels correspond to statistical averaging with the function $W(t)$ from (6), whereas the label 0 denotes averaging with respect to the equilibrium distribution (7). The equation of motion of the vector $\mathbf{m}$ is obtained after multiplying (6) on the left by $\mu\mathbf{e}$ and integrating over angles:

$$2\tau\partial m_i/\partial t = -\mu\{(k_B T)^{-1}\langle(\hat{P}_k U)(\hat{J}_k e_i)\rangle + \langle(\hat{P}_k\ln W)(\hat{J}_k e_i)\rangle\}; \tag{9}$$

the parentheses in Eq. (9) indicate that each operator acts only on the function standing alongside it.

We note that Eq. (9) is an unclosed system of equations with respect to the quantities $m_i \propto \langle e_i\rangle$ to be found whenever the energy function $U(\mathbf{e})$ differs from a constant, since moments of higher order appear on its right side in addition to $\langle e_i\rangle$, e.g., $\langle e_i e_k\rangle$, etc. The problem of decoupling a system of nonstationary moment equations does not have an exact solution, which is a source of considerable difficulty even in calculating the linear response. In what follows, we will use the closure procedure (the so-called effective-field method) first applied to the study of superparamagnet dynamics in Refs. 8, 9, and 16. The mathematical nature of the effective-field approximation identifies it as one of the variants of the well-known Galerkin method.

Let us write the solution to the kinetic equation (6) in the form

$$W \propto \exp[-U_0/k_B T + (\mathbf{ae})], \tag{10}$$

where we assume that the vector parameter (the effective field) $a_k \sim \mu h/k_B T \ll 1$ to be determined is independent of $\mathbf{e}$. Linearization and normalization of the function (10) leads to a form

$$W = W_0[1 + (4\pi/3)^{1/2} a_k(Y_{1k}^* - \langle Y_{1k}^*\rangle_0)]. \tag{11}$$

The spherical harmonics Y_{1k} appear in Eq. (11) because we have chosen to represent vectors in terms of their spherical components ($k = 0, \pm 1$) here and in what follows. In particular, we have for the unit vector $\mathbf{e}$

$$e_k = (4\pi/3)^{1/2} Y_{1k}(\vartheta, \varphi), \quad \langle e_k\rangle = (4\pi/3)^{1/2}\int Y_{1k} W\,d\Gamma,$$

where $d\Gamma = \sin\vartheta\,d\vartheta\,d\varphi$ is the element of solid angle.

We close the equations of motion of the magnetic moment (9) using the effective-field approximation. Substituting (11) into (8) gives a linear relation between the vectors $\mathbf{m}$ and $\mathbf{a}$:

$$m_k = \mu N_{kq} a_q, \quad N_{kq} = (4\pi/3)[\langle Y_{1k} Y_{1q}^*\rangle_0 - \langle Y_{1k}\rangle_0\langle Y_{1q}^*\rangle_0]. \tag{12}$$

Taking the average on the right side of (9) over the distribution function (11), linearizing the result with respect to the small parameter $\mu h/k_B T$, and then eliminating a using (12), we are led to the equation

$$2\tau\partial m_k/\partial t + \Lambda_{kq} m_q = (\mu^2/k_B T) R_{kq} h_q, \tag{13}$$

where the matrix coefficients

$$\Lambda_{kq} = R_{kp} N_{pq}^{-1}, \quad R_{kq} = (4\pi/3)\langle(\hat{J}_s Y_{1k})(\hat{P}_s Y_{1q}^*)\rangle_0 \tag{14}$$

contain averages only with respect to the equilibrium distribution.

It is obvious that Eq. (11) is the simplest type of approximation for the distribution function that is linear in the perturbations. If we use a multiparameter function to solve Eq. (6), e.g.,

$$W = W_0\left\{1 - \sum_{j=1}^{\nu}\left[\sum_{k=-j}^{j} a_{jk}(Y_{jk}^* - \langle Y_{jk}^*\rangle_0)\right]\right\}, \tag{15}$$

where all the a_{jk} are $\sim\mu h/k_B T$, then a closure procedure analogous to (12) and (14) leads to $\nu(\nu+2)$ matrix equations for the coefficients a_{jk}. There is interest in the problem of choosing the minimum value of $\nu_{\min}$ that provides a correct description of FMR in a single-domain particle. Comparing the results of Refs. 8 and 9 shows that the necessary order of approximation depends on the symmetry of the magnetizing field $\mathbf{H}_r = -\partial U/\partial\boldsymbol{\mu}$, which determines the equilibrium orientation of the magnetic moment. Thus, in studying FMR in an external field $\mathbf{H}_r = \mathbf{H}$ (i.e., dipole symmetry), it is permissible to retain only terms with $\nu = 1$ in the sum (15) (see Refs. 9 and 11). For the case of natural FMR i.e., a magnetically uniaxial particle with $\mathbf{H} = 0$ and

hence a field $\mathbf{H}_r$ with quadrupole symmetry, it is necessary (see Ref. 8) to save terms with both $\nu = 1$ and 2 in (15) in order to obtain the correct description. In their numerical solution to this problem, the authors of Ref. 17 also included higher harmonics ($\nu \leqslant 20$). However, they observed that broadening the basis in this way led only to a quantitative refinement of their results compared to those found analytically in Ref. 8 for $\nu_{\min} = 2$.

The considerations we have outlined here clarify the reason for choosing the approximation (11) and determine the range of applicability of Eq. (13) based on it. This equation remains correct provided that the anisotropy field of the particle H_a is small compared to the magnetizing field H, which is the case we will discuss in this paper.

2. FREE OSCILLATIONS OF THE MAGNETIC MOMENT

Let us use Eq. (13) to determine the resonance frequency and damping rate for the precession of the magnetic moment of a single-domain particle, i.e., we set $h = 0$ and compute the eigenvalues of the matrix Λ_{kq} from (14). We choose the z-axis of the coordinate system in the direction of the magnetizing field $\mathbf{H}$, and introduce the notation $x = \cos\vartheta$, where ϑ is the polar angle of the vector $\mathbf{e}$. In order to find the matrix elements, we make use of the identity

$$(\hat{J}_h u)(\hat{J}_h v) = \frac{\partial u}{\partial \vartheta}\frac{\partial v}{\partial \vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial u}{\partial \varphi}\frac{\partial v}{\partial \varphi},$$
$$(\hat{J}_h u)(\nabla_h v) = \frac{1}{\sin\vartheta}\left[\frac{\partial u}{\partial \vartheta}\frac{\partial v}{\partial \varphi} - \frac{\partial u}{\partial \varphi}\frac{\partial v}{\partial \vartheta}\right],$$

where u,v are arbitrary angular functions. For the diagonal components of the matrices N_{kp} and R_{kp} we find from (12) and (14) that

$$N_0 \equiv N_{00} = \langle x^2\rangle_0 - \langle x\rangle_0^2, \quad N_\pm \equiv N_{\pm 1,\pm 1} = {}^1/_2(1 - \langle x^2\rangle_0), \tag{16}$$
$$R_0 \equiv R_{00} = 1 - \langle x^2\rangle_0, \quad R_\pm \equiv R_{\pm 1,\pm 1} = {}^1/_2[1 + \langle x^2\rangle_0 \mp (2i/\alpha)\langle x\rangle_0].$$

Let us first investigate the case of a magnetically isotropic particle when the equilibrium distribution function W_0 from (7) contains only a contribution associated with the magnetizing field:

$$U_0 = -\mu(\mathbf{eH}) = -\mu H x.$$

Because of the uniaxial symmetry of $W_0(x)$, the matrices N_{kp} and R_{kp} are found to be diagonal, and their nonzero elements

$$N_0 = dL_1/d\xi, \quad N_\pm = L_1/\xi, \quad R_0 = 2L_1/\xi, \quad R_\pm = 1 - L_1/\xi \mp iL_1/\alpha \tag{17}$$

are expressed in a simple way in terms of the Langevin function;

$$L_1(\xi) = \coth\xi - 1/\xi, \quad \xi = \mu H/k_B T.$$

For the eigenvalues of $\Lambda_{kq} = \lambda_k \delta_{kq}$ we obtain from (14) and (17)

$$\lambda_0 = 2(d\ln\xi/d\ln L_1), \quad \lambda_\pm = \xi/L_1 - 1 \mp i\xi/\alpha. \tag{18}$$

Substituting (18) into (13) for $h = 0$, we find the frequency of free precession ω_0 and relaxation time $\tau_\perp$ for the component of the magnetic moment perpendicular to $\mathbf{H}$:

$$\omega_0 = |\operatorname{Im}\lambda_\pm|/2\tau = \xi/2\alpha\tau = \gamma H,$$
$$\tau_\perp = 2\tau/\operatorname{Re}\lambda_\pm = 2\tau L_1(\xi - L_1)^{-1} = (\alpha\gamma H)^{-1}\xi L_1(\xi - L_1)^{-1}. \tag{19}$$

Equation (19) reproduces the results of Ref. 9. This equation implies that the precession frequency of an isotropic superparamagnet always remains the same as in the bulk crystal, while the relaxation time decreases without bound as the argument of the Langevin function ξ decreases, i.e., with increasing temperature or decreasing particle size. In what follows it is convenient to write the relaxation time in the form $\tau_\perp = (\alpha_e \gamma H)^{-1}$, introducing an effective damping rate for the precession

$$\alpha_e = \alpha(\xi - L_1)/\xi L_1 = \begin{cases} 2\alpha/\xi, & (\xi \ll 1), \\ \alpha, & (\xi \gg 1). \end{cases} \tag{20}$$

We now turn to the case of particles that possess a nonzero magnetic anisotropy (due either to crystallography or an anisotropic shape), i.e., we consider an energy function of the form $U = U_0 + U_a$. For the anisotropy contribution U_a it is convenient to use the representation[18]

$$U_a = -V\sum_{j\,\text{even}}^{\infty} K_j \Phi_j(\mathbf{e}), \quad \Phi_j = \sum_{m=-j}^{j} b_m Y_{jm}(\vartheta', \varphi'), \tag{21}$$

where the K_j are anisotropy constants, b_m are numerical coefficients, and ϑ' and φ' are angles the magnetic moment vector of the particle makes with the anisotropy axis. In the approximation of weak anisotropy, when we have $|U_a|/\mu H \ll 1$, the first-order corrections to the eigenvalues of Eq. (13) can be obtained if we use for the equilibrium distribution function the expression

$$W_e = W_0\left\{1 + \frac{V}{k_B T}\sum_j K_j[\Phi_j(\mathbf{e}) - \langle\Phi_j(\mathbf{e})\rangle_0]\right\}, \tag{22}$$

where W_0 is the "Langevin-like" distribution function from (7). Taking into account contributions linear in K_j does not alter the diagonal nature of the matrix Λ_{kp}, since the calculation of the decay rates λ_k reduces to finding the equilibrium moments $\langle x\rangle_e$ and $\langle x^2\rangle_e$ with the distribution function (22) and substituting them into Eq. (16) in place of $\langle x\rangle_0$ and $\langle x^2\rangle_0$.

Let us note that in calculating the moments $\langle\ldots\rangle_e$ it is necessary to transform the angular coefficients $\Phi_j(\mathbf{e})$ of the expansion (21) to the coordinate system in use, for which the polar axis is directed along the magnetizing field $\mathbf{H}$. Since we require only the convolution of $\Phi_j(\mathbf{e})$ with functions that do not contain any azimuthal dependence, it is sufficient for their calculation to use the integral relations obtained in Ref. 18:

$$\langle P_j(x)\Phi_{j'}(\mathbf{e})\rangle_0 = \langle P_j(x)P_{j'}(x)\rangle_0 \Phi_{j'}(\Gamma), \tag{23}$$

where $P_j(x)$ is a Legendre polynomial of the argument $x = \cos\vartheta$, and $\Phi_j(\Gamma)$ is the angular representation of Φ_j in the coordinate system bound to $\mathbf{H}$.

Averaging with the distribution function (22) gives the following expression for the eigenvalues of Eq. (13):

$$\lambda_k = \lambda_k^{(0)} + \Delta\lambda_k = \lambda_k^{(0)} + (\Delta R_k - \lambda_k^{(0)}\Delta N_k)/N_k^{(0)}, \tag{24}$$

where $\lambda_k^{(0)}$ and $N_k^{(0)}$ are defined by Eqs. (17) and (18). Calculating the corrections $\Delta\lambda$ and ΔN using Eq. (23) gives

$$\Delta R_0 = -(V/k_BT)\sum_j K_j\Phi_j(\Gamma)\langle x^2P_j\rangle_0,$$
$$\Delta R_\pm = (V/2k_BT)\sum_j K_j\Phi_j(\Gamma)\langle (x^2\mp 2(i/\alpha)x)P_j\rangle_0, \quad (25)$$
$$\Delta N_0 = (V/k_BT)\sum_j K_j\Phi_j(\Gamma)\langle x^2-2\langle x\rangle_0 P_j\rangle_0,\ \Delta N_\pm = \Delta R_0/2.$$

Substituting (25) into (24) gives

$$R_+ = \left(1-\frac{L_1}{\xi}-\frac{i}{\alpha}L_1\right)+\frac{V}{k_BT}\sum_j K_j\Phi_j \times\left\{\left[\frac{j(j+1)}{2\xi^2}-\frac{1}{\xi}\frac{dL_j}{d\xi}\right]-\frac{i}{\alpha}\frac{dL_j}{d\xi}\right\}, \quad (26)$$

which allows us to represent the eigenvalues in the form

$$\lambda_\pm = \left\{\frac{\xi}{L_1}-1+\frac{V}{k_BT}\sum_j\frac{1}{L_1^2}\left\{\frac{j(j+1)}{2}L_j-\xi\frac{dL_j}{d\xi}\right]K_j\Phi_j\right\} \mp i\left\{\frac{\xi}{\alpha}+\frac{V}{\alpha k_BT}\sum_j\frac{j(j+1)}{2}\frac{L_j}{L_1}K_j\Phi_j\right\}, \quad (27)$$

where $L_j \equiv \langle P_j\rangle_0$; the explicit expression for λ_0 will not be given here due to its complexity. In deriving Eqs. (26) and (27) we made use of the relation

$$\langle(1-x^2)P_j(x)\rangle_0 - \frac{2}{\xi}\langle xP_j(x)\rangle_0 + \frac{j(j+1)}{\xi^2}\langle P_j(x)\rangle_0 = 0,$$

obtained by averaging the equations for the Legendre polynomials with the distribution function W_0 from (7).

The free precession parameters of an anisotropic superparamagnetic particle can be found by substituting (27) into the definition (19). Let us do this for the two best-known types of anisotropy, uniaxial ($j=2, K_2=K_u$) and cubic ($j=4, K_4=K_c$). In these cases the sums entering into expressions (26)–(27) contain only one nonzero term:

$$K_j\Phi_j(\Gamma) = \begin{cases} \frac{2}{3}K_uP_2(\cos\vartheta)\delta_{2j}, \\ \frac{2\pi^{1/2}}{15}K_c\left[Y_{40}(\vartheta,\varphi)+\left(\frac{5}{14}\right)^{1/2}(Y_{44}(\vartheta,\varphi)+Y_{4,-4}(\vartheta,\varphi))\right]\delta_{4j}. \end{cases} \quad (28)$$

Here the angle $\Gamma = \{\vartheta,\varphi\}$ gives the position of the anisotropy axis of the particle in a spherical system of coordinates with the polar axis along the field **H**. Using Eq. (28), we obtain from (27) the eigenfrequencies of oscillation of the magnetic moment:

$$\omega_0^{(u)} = \gamma\left[H+2\frac{K_u}{M_s}\frac{L_2}{L_1}P_2(\cos\vartheta)\right],$$
$$\omega_0^{(c)} = \gamma\left[H+2\frac{K_c}{M_s}\frac{L_4}{L_1}\left(1-\frac{5}{4}\sin^2 2\vartheta-\frac{5}{4}\sin^4\vartheta\sin^2 2\varphi\right)\right]. \quad (29)$$

It follows from Eq. (27) that in small particles a thermal-fluctuation-induced "dressing" of the anisotropy constant of the form $\tilde{K}_j \approx K_j(L_j/L_1)$ takes place; as the temperature increases, for $\xi < 1$ the anisotropy "melts" according to the law $\tilde{K}_j \propto \xi^{j-1}$. For crystallographic anisotropy this dependence was predicted from intuitive considerations in Ref. 10. However, for uniaxial anisotropy caused by the shape of a particle the authors of Ref. 10 obtained a different result: $\tilde{K}_j \approx K_jL_1$. This is obviously an error, since according to the rigorously obtained expressions (25)–(29) the renormalization $\tilde{K}_j \approx K_j(L_j/L_1)$ should not depend on the specific nature of the anisotropy constants.

3. DYNAMIC SUSCEPTIBILITY OF AN ENSEMBLE OF SUPERPARAMAGNETIC PARTICLES WITH A RANDOM DISTRIBUTION OF ANISOTROPY AXES

In order to calculate the response of a particle to a weak time-dependent field **h** it is necessary to use the inhomogeneous equation (13). As is well-known, the fundamental characteristic of FMR is the susceptibility χ_+ with respect to a circularly polarized field

$$\mathbf{h} = (h_0/2^{1/2})(\cos\omega t,\ \sin\omega t,\ 0),$$

whose direction of rotation coincides with the direction of free precession of the magnetic moment. The complex form of the description of **h** in terms of the spherical components is especially simple:

$$\mathbf{h} = (h,\ 0,\ 0),\quad h = h_0\exp(i\omega t). \quad (30)$$

After substituting (30) into (13) and (14) we obtain the dynamic susceptibility of the particle in the form

$$\chi_+(\omega) = (\mu^2/k_BT)R_+(2i\omega\tau+\lambda_+)^{-1}, \quad (31)$$

where R_+ and λ_+ are defined by expressions (26) and (27). We note that the function $\chi_+(\omega)$ depends parametrically on the angular coordinates of the anisotropy axis of the particle.

In a solid dispersed ferromagnet the direction of the anisotropy axes of the particles is fixed and determines the stable orientation of the texture. In order to describe the latter it is necessary to use the distribution function $f(\Gamma)$ normalized by the condition

$$\int f(\Gamma)\,d\Gamma = n,$$

where n is the number of particles in a unit volume of the material. The susceptibility of such an ensemble is obtained by averaging the quantity (29) with respect to the distribution of anisotropy axes:

$$\bar{\chi}_+ = \int\chi_+ f(\Gamma)\,d\Gamma \quad (32)$$

for an ideally oriented system, where $f(\Gamma) = n\delta(\Gamma-\Gamma_0)$, the averaging reduces to multiplying by n, so that

$\bar{\chi}_+ = n\chi_+(\Gamma_0)$. In all the remaining cases it is necessary to calculate the angular integral (32) in order to find $\bar{\chi}_+$.

Let us calculate the susceptibility for a case that is often encountered in practice: that of an isotropic ($f = \text{const}$) distribution of particle anisotropy axes. This orientational texture is characteristic of dispersed ferromagnets that are fabricated without applying an external field, e.g., dispersively solidified alloys of the Cu–Co type, granular ferromagnetic films, magnetic liquids that are frozen or polymerized, etc.

We note that in a system of randomly oriented particles the spread in resonant frequencies associated with the fact that the internal fields $H_a \sim K/M_s$ of the particles point in different directions with respect to the magnetizing field is a maximum. The contribution to the resonance linewidth $\Delta\omega \sim \gamma H_a$ due to this spread is often much larger than the corresponding linewidth $\Delta\omega \sim \alpha\gamma H$ of the FMR line of the particle material. This orientational "inhomogeneous" broadening plays an important role in forming the magnetic spectra of polycrystalline ferrites.[7] A theory of inhomogeneous broadening—the "independent grain model"—was constructed in Refs. 19 and 20 without taking into account fluctuations of the magnetic moments. Our approach generalizes this model to the case of superparamagnetic particles.

It is not difficult in principle to calculate the integral (32) from the function (29), although the result often turns out to be very cumbersome (see the explicit expressions for R_+ and λ_+). In particular, the integral can be performed analytically for the case of uniaxial anisotropy. Substitution of (26), (30), and (31) into (32) and integration over angles gives

$$\bar{\chi}_+ = \frac{n\mu^2}{k_B T}\left\{\frac{B}{D} + \left[\frac{2A-B}{2C-D} - \frac{B}{D}\right]\frac{\operatorname{arctg}[3D/(2C-D)]^{1/2}}{[3D/(2C-D)]^{1/2}}\right\}, \tag{33}$$

where the function arctan and the expressions within the 1/2 power signs must be understood in the sense of analytic continuations, because the coefficients

$$A = 1 - \left(\frac{1}{\xi} + \frac{i}{\alpha}\right)L_1, \quad B = \frac{2K_u V}{3k_B T}\left[\frac{3}{\xi^2} - \left(\frac{1}{\xi} + \frac{i}{\alpha}\right)\frac{dL_2}{d\xi}\right],$$

$$C = 2i\omega\tau + \left(\frac{\xi}{L_1} - 1\right) - \frac{i}{\alpha}\xi, \tag{34}$$

$$D = \frac{2K_u V}{3k_B T}\frac{1}{L_1^2}\left(3 - \xi\frac{d}{d\xi} - 3\frac{i}{\alpha}L_1\right)L_2$$

are complex quantities.

Equation (33) allows us to take various limits that lead to familiar expressions. Let us do this, e.g., for the imaginary part of the dynamic susceptibility $\bar{\chi}_+ = \bar{\chi}'_+ + i\bar{\chi}''_+$.

1) For $K_u \to 0$ we immediately obtain the result of Ref. 9

$$\bar{\chi}_+'' = \frac{n\mu^2}{k_B T}\frac{\operatorname{Re} A \operatorname{Im} C - \operatorname{Im} A \operatorname{Re} C}{|C|^2} = \gamma M \frac{\alpha_e \omega}{(\omega-\omega_H)^2 + \alpha_e^2\omega_H^2}, \tag{35}$$

where $M = n\mu L_1(\xi)$, $\omega_H = \gamma H$, and the effective damping rate is determined by Eq. (20). Since the parameter α_e reduces to α as $\xi \to \infty$, the classical result for χ_+ of an isotropic ferromagnet at low temperatures (or for large-volume particles) follows from (35).

2) In the limit of particles made of a material with a vanishingly small ($\alpha \to 0$) intrinsic FMR linewidth, only those particles for which the resonance condition (29) holds contribute to the observed susceptibility (32). Particles oriented with anisotropy axes transverse to the magnetizing field ($\vartheta = \pi/2$) have the lowest resonance frequency: $\omega_r = \omega_H(1 - \varepsilon L_2/L_1)$, where $\varepsilon = K_u/M_s H$. This quantity determines the left-hand edge of the absorption curve on the frequency axis. The right-hand edge of the function $\bar{\chi}''_+$, i.e., the largest resonance frequency, is given in this case by $\omega_r = \omega_H(1 + 2\varepsilon L_2/L_1)$, which corresponds to $\vartheta = 0$. Thus, the intrinsic inhomogeneous broadening of the absorption line is

$$\Delta\omega = 3\varepsilon\omega_H L_2/L_1. \tag{36}$$

Taking the limit $\alpha \to 0$ in Eq. (33), in that frequency interval we obtain

$$\bar{\chi}_+'' = \frac{\pi M}{2H}\frac{1 + (1 - L_1^2/L_2)(1 - \omega/\omega_H)}{[(3|\varepsilon|L_2/L_1)(\omega/\omega_H + \varepsilon L_2/L_1 - 1)]^{1/2}}. \tag{37}$$

It is clear from (37) that the absorption curves for particle ensembles with positive and negative anisotropies ($\varepsilon > 0, \varepsilon < 0$) are mapped into each other under reflection with respect to the axis $\omega = \omega_H$. At low temperatures ($\xi \to \infty$) there follows from (37) the expression

$$\bar{\chi}_+'' = \frac{\pi M}{2H}\frac{1}{[3|\varepsilon|(\omega/\omega_H + \varepsilon - 1)]^{1/2}}, \tag{38}$$

defined in the interval $1 - \varepsilon < \omega/\omega_H < 1 + 2\varepsilon$. Eq. (38), which is obtained from (33) in the limits $\alpha \to 0$ and $\xi \to \infty$, corresponds to the results of Morrison and Karayianis[19] for an ensemble of independent uniaxial weakly anisotropic ferromagnetic grains.

Figures 1 and 2 show the results of calculations of $\bar{\chi}''_+$ for finite values of α, ε, and ξ when the particles have uniaxial and cubic anisotropy. The situation here is typical of experiments in which the frequency ω and amplitude h_0 of the AC field are fixed. The parameters that vary are the dimensionless intensity of the magnetizing field $\gamma H/\omega$ and the quantity $\xi_0 = M_s V\omega/\gamma k_B T$, which is analogous to ξ and is determined by the particle size and temperature. Let us take $\alpha = 10^{-2}$ for the FMR linewidth of the particle material, and choose the anisotropy parameter in the form $\varepsilon = K\gamma/M_s\omega$, where K is the uniaxial or cubic anisotropy constant respectively.

Let us indicate the characteristic ranges of values of ξ_0 and ε, assuming that $M_s \approx 500$ G and $K \sim 10^5$ erg/cm (magnetite), and $\omega = 2\pi \cdot 10^{10}$ rad/sec (i.e., a spectrometer wavelength of 3 cm. From this we find that when $\gamma = 2 \cdot 10^7$ erg/Oe, ξ_0 varies from ~ 1 (particles of diameter ~ 50 Å, temperature ~ 400 K) to ~ 100 (particle diameter ~ 150 Å, temperature ~ 100 K). For the same values of the magnetic characteristics we find $|\varepsilon| \approx 0.1$ for the anisotropy parameter, independent of the particle size. These estimates give a feeling for how closely the spectral curves of Figs. 1 and 2 correspond to an actual disperse ferromagnet.

For convenience and clarity we present not only the family of absorption lines $\bar{\chi}''_+$, but also their derivatives $d\bar{\chi}''_+/dH$. The latter are directly proportional to the signal recorded by the spectrometer, and are also convenient for

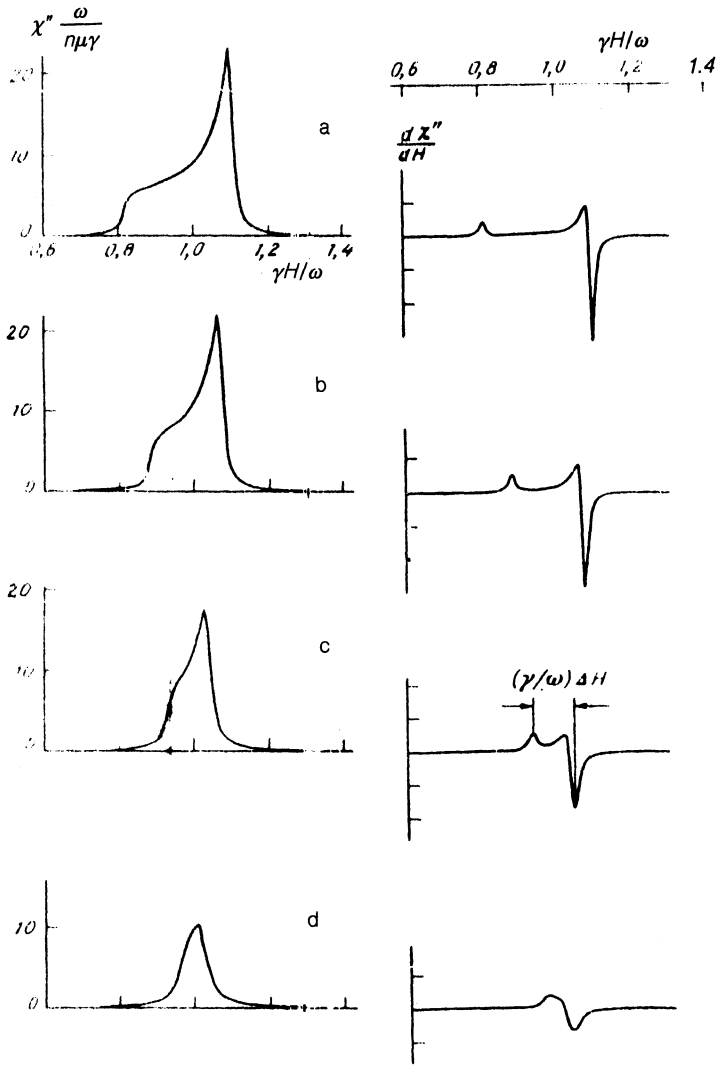

FIG. 1. Absorption line shape $\bar{\chi}''_+$ (left column) and $d\bar{\chi}''_+/dH$ (right column) for an ensemble of particles with positive uniaxial anisotropy ($\varepsilon = 0.1$) as functions of the Langevin parameter: $\xi_0 = 50$ (a), 5 (b), 2 (c), and 1 (d); for all the curves the precession attenuation parameter $\alpha = 10^{-2}$

finding the exact width ΔH of the FMR line. The quantity ΔH is defined as the distance along the field axis between the two extrema (maximum and minimum) of the function $d\bar{\chi}''_+/dH$ located on different sides of the point $d\bar{\chi}''_+/dH = 0$ that are farthest away from this point. We note that according to this definition the width of a symmetric Lorentzian line (35) is $\Delta H = 2\alpha_e\omega/3^{1/2}\gamma$.

Figures 1 and 2 allow us to trace how the line shape changes as the temperature increases, i.e., as ξ_0 decreases. A curve for $\bar{\chi}''_+$ that is initially asymmetric with clearly marked and steep edges and a width $\Delta H \approx 3\varepsilon\omega/\gamma$ gradually is transformed into a smooth symmetric Lorentzian curve. In this case the maximum absorption shifts to the point $\gamma H/\omega = 1$, corresponding to magnetic resonance in an isotropic superparamagnet. The smoothing of the curve is easy to understand if we recall that as the temperature increases the inhomogeneous broadening of the line (36) decreases and the effective attenuation constant α_e given in (20) increases, and that the latter determines the homogeneous broadening. To sum up, we are led to conclude that in a randomly oriented disperse ferromagnet the absorption linewidth turns out to be a nonmonotonic function of temperature. For low temperatures ΔH is large due to the scatter in directions of the anisotropy fields of the particles (inhomogeneous broadening); as the temperature increases the thermally induced tendency to make the magnet isotropic causes ΔH to decrease, but in the fluctuation region it once again begins to increase. This effect is illustrated in Figs. 3a and 3b, which show our numerical calculations of the dependence of ΔH on $\xi_0 \propto 1/T$ for randomly oriented uniaxial and cubic magnets. In the same figures we compare the behavior of this function with the following asymptotically exact solutions, shown as dashed curves: $(\gamma/\omega)\Delta_s H = 2\alpha_e/3^{1/2}$ for superparamagnetic broadening (as $K \to 0$), $(\gamma/\omega)\Delta_u H = 3\varepsilon L_2/L_1$ for inhomogeneous broadening as $\alpha \to 0$ for the case of uniaxial anisotropy, and $(\gamma/\omega)\Delta_c H = 10/3\ \varepsilon L_4/L_1$ for inhomogeneous broadening as $\alpha \to 0$ in the case of cubic anisotropy. It is remarkable how rapidly the exact solution approaches the corresponding asymptotic curves on both sides of the minimum point, independent of the type of magnetic anisotropy. It is clear from Fig. 3 that the position of this point can be estimated using the relations $\Delta_s H = \Delta_u H$ and $\Delta_s H = \Delta_c H$. It is especially simple to obtain estimates for the case of uniaxial anisotropy.

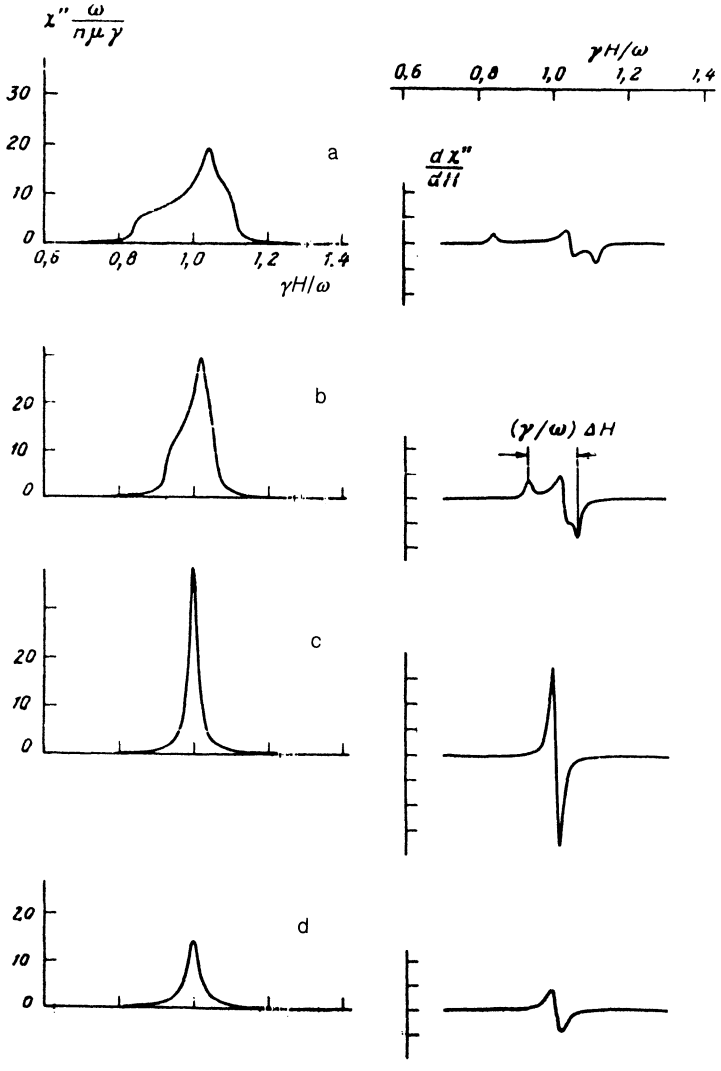

FIG. 2. Absorption line shape $\bar{\chi}''_+$ (left column) and $d\bar{\chi}''_+/dH$ (right column) for an ensemble of particles with positive cubic anisotropy ($\varepsilon = 0.1$) as functions of the Langevin parameter: $\xi_0 = 50$ (a), 10 (b), 2 (c), and 1 (d); for all the curves the precession attenuation parameter $\alpha = 10^{-2}$.

For definiteness, let us use the asymptotic forms (35) and (36) to write the expressions for the superparamagnetic and inhomogeneous contributions to the linewidth of an ensemble of magnetically uniaxial particles:

$$\Delta_s H = \frac{2}{3^{1/2}} \frac{\omega}{\gamma} \alpha \frac{\xi_0 - L_1}{\xi_0 L_1}, \quad \Delta_u H = 3 \frac{\omega}{\gamma} \varepsilon \frac{L_2}{L_1}, \tag{39}$$

and investigate these expressions when $\xi_0 < 1$. An expansion gives

$$\Delta_s H = \frac{4}{3^{1/2}} \frac{\omega}{\gamma} \frac{\alpha}{\xi_0}, \quad \Delta_u H = \frac{3}{5} \frac{\omega}{\gamma} \varepsilon \xi_0.$$

Setting $\Delta_s H = \Delta_u H$, we obtain the relation

$$\xi_0^{(min)} = 2(5\alpha/3^{4/5}\varepsilon)^{1/2}, \quad (\gamma/\omega)\Delta H^{(min)} = 4(3^{1/2}\alpha\varepsilon/5)^{4/5},$$

which is in satisfactory agreement with the results of the numerical calculations.

The results of including the effects of both superpara-

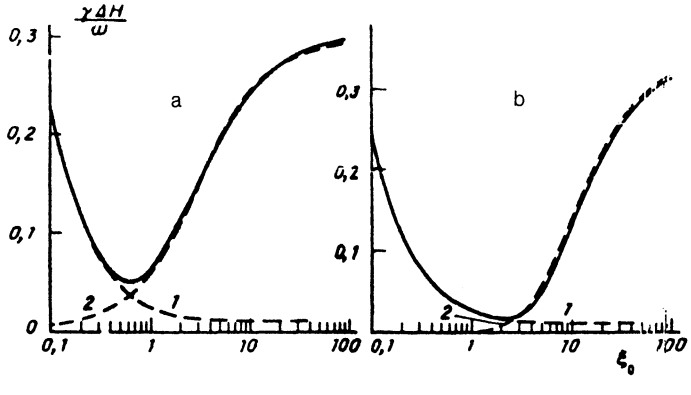

FIG. 3. FMR linewidth of an ensemble of randomly oriented particles as a function of their Langevin parameter $\xi_0 \propto 1/T$ for the cases of uniaxial (a) and cubic (b) anisotropy when $\alpha = 10^{-2}$, $|\varepsilon| = 0.1$. The solid curves are numerical calculations, the dashed curves show the asymptotic dependence of $\Delta_s H$ (*1*) and $\Delta_u H$ (*2* in Fig. a), $\Delta_c H$ (*2* in Fig. b).

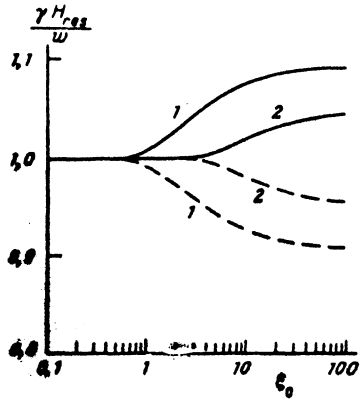

FIG. 4. Position of the maximum of the curve $\bar{\chi}''_+$ (resonance field) as a function of the Langevin parameter $\xi_0 \propto 1/T$ for uniaxial (curve *1*) and cubic (curves *2*) anisotropy when $\varepsilon = 0.1$ (solid curves) and $\varepsilon = -0.1$ (dashed curves).

magnetic and inhomogeneous broadening on the value of the resonance field H_{res}, which we determine based on the position of the point $d\bar{\chi}''_+/dH = 0$, i.e., that of the peak in the absorption curve, are illustrated in Fig. 4. It turns out that heating the sample can lead to either an increase or a decrease in the resonance field, depending on the sign of the magnetic anisotropy constant of the particles.

4. CONCLUSIONS

In randomly oriented dispersed ferromagnets and ferrites, superparamagnetism can weaken or entirely suppress the inhomogeneous broadening of the FMR line caused by the scatter in orientations of the anisotropy axis.

In such systems the combined influence of the orientational texture and the superparamagnetism can lead to a nonmonotonic temperature dependence of the FMR linewidth, of the sort that has been noted in a number of experiments when the latter is measured in a magnetizing field, i.e., $\Delta H(T)$ passes through a minimum for $T \sim (V/k_B)(KM_s\omega/\alpha\gamma)^{1/2}$.

The character of the temperature dependence of the resonance field is connected in a simple way with the nature and sign of the magnetic anisotropy of the particles in the dispersed ferromagnet: as the temperature decreases, H_{res} increases for systems with $K > 0$ and decreases for the case $K < 0$.

[1] D. L. Griscom, IEEE Trans. Magn. **17**, 2718 (1981).
[2] F. Schmidt and T. Meeder, Surf. Sci. **106**, 397 (1981).
[3] M. I. Shliomis and Yu. L. Raikher, IEEE Trans. Magn. **16**, 237 (1980).
[4] G. A. Petrakovskii, V. I. Piskorskii, V. M. Sosnin *et al.*, Fiz. Tverd. Tela (Leningrad) **25**, 3256 (1983) [Sov. Phys. Solid State **25**, 1876 (1983)].
[5] *Biogenic Magnetite and Magnetoretention* (in Russian), G. Kirshwink, D. Jones and B. MacFallen (eds.), Mir, Moscow, 1989.
[6] L. Néel, Comptes Rendues de l'Acad. Sci., Paris, **228**, 664 (1949).
[7] A. G. Gurevich, *Magnetic Resonance in Ferrites and Antiferromagnets* (in Russian), Nauka, Moscow, 1973.
[8] Yu. L. Raikher and M. I. Shliomis, Zh. Eksp. Teor. Fiz. **67**, 1060 (1974) [Sov. Phys. JETP **40**, 526 (1975)].
[9] R. S. Gekht, V. A. Ignatchenko, Yu. L. Raikher *et al.*, Zh. Eksp. Teor. Fiz. **70**, 1300 (1976) [Sov. Phys. JETP **43**, 677 (1976)].
[10] R. S. de Biasi and T. C. Devezas, J. Appl. Phys. **49**, 2466 (1978).
[11] V. I. Stepanov and M. I. Shliomis, *Physical Properties of Magnetic Liquids* (in Russian), p. 89. Sverdlovsk: Ural Sci. Center, USSR Acad. Sci., 1983.
[12] D. M. S. Bagguley and N. J. Harrick, Proc. Phys. Soc. A **67**, 648 (1954).
[13] I. M. Batyev and A. N. Kozlova, *Physical Properties and Hydrodynamics of Dispersed Ferromagnets* (in Russian), p. 58. Sverdlovsk: Ural Sci. Center, USSR Acad. Sci., 1977.
[14] V. K. Sharma and A. Baiker, J. Chem. Phys. **75**, 5596 (1981).
[15] S. Engels and W. Mörke, Phys. Status Solidi B **119**, K109 (1983).
[16] M. A. Marenyuk, Yu. L. Raikher and M. I. Shliomis, Zh. Eksp. Teor. Fiz. **65**, 834 (1973) [Sov. Phys. JETP **38**, 413 (1973)].
[17] Yu. L. Raikher and V. I. Yakushin, *Nonequilibrium Processes in Magnetic Suspensions* (in Russian), p. 78. Sverdlovsk: Ural Sci. Center, USSR Acad. Sci., 1985.
[18] H. B. Callen and E. R. Callen, J. Phys. Chem. Solids **27**, 1271 (1966).
[19] C. A. Morrison and N. Karayianis, J. Appl. Phys. **29**, 339 (1958).
[20] E. Schlömann and J. R. Zeender, J. Appl. Phys. **29**, 341 (1958).

Translated by Frank J. Crowne