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Contents.

INTRODUCTION.

A great number of effective methods of investigation of thermal and dissipative properties of different samples have been worked out lately. Many of these methods are based on the measurement of the value of thermoelastic oscillations appearing in the volume of the substance under investigation during the absorption of modulated light radiation by the substance. One of these methods is the method of photodeflection spectroscopy [1], which exhibits great sensitivity even to small changes of temperature. In the present paper the method of photodeflection spectroscopy is used for the investigation of the dissipative properties of magnetic fluids.

Magnetic fluids [2] are ultradisperse stable colloidal solutions of ferro- or ferrimagnetic one-domain particles, dispersed in different fluids. Magnetic permittivity μ of such colloids reaches ~ 10, while in usual fluids $\mu \ll 1$ [3]. While magnetized by the external field the orientation ordering of particles takes place and the colloid shows anisotropy with respect to its optical and dissipative properties [4]. Magnetic fluids absorb electromagnetic radiation in the visible range of wavelengths to a great extent, therefore investigation of magneto-optic effects is usually carried on for diluted colloidal solutions with volume concentration $c \sim 10^{-5} - 10^{-3}$ and for slight thicknesses [2].

The use of photodeflection spectroscopy for the investigation of thermal and dissipative properties of magnetic fluids is based on the following characteristic peculiarities of the present method:

– the mechanic contact with the investigated sample is absent;

– the method of photodeflection spectroscopy is essentially three-dimensional;

– derivatives of temperature with respect to spatial coordinates are used in computations, which substantially simplifies calculations in the case of non-homogeneous samples [5].

The method of photodeflection spectroscopy is based on the following principles [6]: the exciting laser beam passes through the sample and the wavelength of the exciting radiation is chosen in the band of absorption of particles of the sample under investigation; the particles absorb light energy, part of which is transformed into oscillatory- rotational modes, that is into heat; the local change of medium temperature leads to the appearance of the gradient of the refractive index, which is registered by the probe laser beam of small power; one can estimate the optic, dissipative and thermal characteristics of the sample under investigation judging by the angular value of deflection of the probe beam during its passing through the region with non-homogeneous refractive index.

On the basis of the method of photodeflection spectroscopy and similar

method of thermal lens [7] highly sensitive spectrometers and spectropolarimeters are created nowadays [8]. The minimal value of dichroism registered by these devices is 10^{-4} of absorbance [8].

In the first section of the present paper certain aspects of theory of the method of photodeflection spectroscopy are considered and expressions for the temperature distribution and deflection angles of the probe beam in the magnetic fluid have been received. The second and the third sections deal with numerical calculations and graphic analysis of the value of energy dissipation, thermal fields and angular deflection of the probe beam during the continuous and pulse modulation of exciting radiation as a function of the value of the external magnetic field, the shape of the particles of the magnetic fluid, the coordinate of the measurement point, the radius of the exciting beam and the time of interaction.

1. THE USE OF THE METHOD OF PHOTODEFLECTION SPECTROSCOPY FOR THE INVESTIGATION OF THERMAL AND DISSIPATIVE PROPERTIES OF MAGNETIC FLUIDS.

Let the laser beam acting on magnetic fluid excite thermoelastic oscillations in the band of absorption. Then the volume dissipation of energy of the light beam can be expressed as follows

$$Q(\mathbf{r},t) = k_0 I(\mathbf{r},t)\exp(-k_0 z), \tag{1.1}$$

where k_0 is the absorption factor of the magnetic fluid, $I(\mathbf{r},t)$ is the intensity of the incident radiation. Taking into account that the laser beam can be considered Gaussian with a great degree of accuracy, we have the following expression for the intensity of radiation:

$$I(\mathbf{r},t) = I_0 \exp\left(-\frac{\mathbf{r}^2}{a^2}\right) f(t). \tag{1.2}$$

Here I_0 is the amplitude of the light wave, $f(t)$ is the function modulating the source, a is the radius of the Gaussian beam.

The dissipation of energy (1.1) is the density of the power of heat sources in the heat conduction equation

$$\Delta T(\mathbf{r},t) - \frac{1}{\beta_s}\frac{\partial}{\partial t} T(\mathbf{r},t) = -\frac{1}{k_s} Q(\mathbf{r},t), \tag{1.3}$$

which describes the temperature distribution in the magnetic fluid. In the equation (1.3) k_s is thermal conductivity connected with thermal diffusivity β_s by the ratio $\beta_s = k_s/\rho C_p$, ρ is density, C_p is specific heat. For two-phase system [3]

$$k_s = k_c \frac{2k_c + k_p - 2c(k_c - k_p)}{2k_c + k_p + c(k_c - k_p)}, \tag{1.4}$$

where c is the volume concentration of the solid phase, k_c and k_p are coefficients of heat conduction of carrier media and colloidal particles respectively. In the case of magnetic fluids on the hydrocarbon base in the range of volume concentrations values $0.004 \leq c \leq 0.2$ one can make use of the empirical dependence [3]

$$k_s = a_0 + a_1 c + a_2 c^2, \tag{1.5}$$

where $a_0 = 0.1267$, $a_1 = -0.0559$, $a_2 = 3.455$.

The density of the magnetic fluid when fluid base densities equal those of surface active substance used for the stabilization of colloidal particles,

is determined by the formula [3]

$$\rho = \rho_c + (\rho_p + \rho_c). \tag{1.6}$$

The solution of heat conduction equation (1.3) neglecting temperature dependence of parameters k_*, β_*, ρ, C_p, that is valid at insignificant powers of laser radiation will be sought in the form

$$T(x,y,z,t) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty}\int_{0}^{\infty} \Delta Q(\xi,\eta,\mu,\tau)\, G(\xi,\eta,\mu,\tau)\, d\xi\, d\eta\, d\mu\, d\tau, \tag{1.7}$$

demanding continuity of temperature and thermal flows on the boundary dividing the magnetic fluid and the surroundings as well as fulfillment of standard initial conditions. In (1.7) $G(\xi,\eta,\mu,\tau)$ is the Green function satisfying operator equation

$$\Delta G - \frac{1}{\beta_*}\frac{\partial}{\partial t}G = -\frac{1}{k_*}\,\delta(x-\xi, y-\eta, z-\mu)\,\delta(t-\tau). \tag{1.8}$$

where the delta-function $\delta(x-\xi, y-\eta, z-\mu)\,\delta(t-\tau)$ determines the instantaneous dotted source of heat.

Having fulfilled designation $G(\xi,\eta,\mu,\tau)$ and delta-functions $\delta(x-\xi, y-\eta, z-\mu)$, $\delta(t-\tau)$ into Fourier integral we can obtain the following expression for the Green function of the heat conduction equation (1.3)

$$G = \frac{\Theta(t)}{8\rho C_p \pi^{3/2}(\beta_*(t-\tau))^{3/2}} \times \exp\left[-\frac{(x-\xi)^2}{4\beta_*(t-\tau)}\right] \times \\ \times \exp\left[-\frac{(y-\eta)^2}{4\beta_*(t-\tau)}\right] \times \exp\left[-\frac{(z-\mu)^2}{4\beta_*(t-\tau)}\right], \tag{1.9}$$

where $\Theta(t)$ is the Heaviside unit step function.

Making use of (1.9) and having integrated expression (1.7) by spatial coordinates taking into account the relations (1.1), (1.2) as well as initial and boundary conditions, one can receive the distribution of temperatures in the volume of the magnetic fluid

$$T(x,y,z,t) = \frac{k_0}{2k_*}\int_0^t \frac{f(\tau)}{a^2 + 8\beta_*(t-\tau)} \exp\left[-\frac{2(x^2+y^2)}{a^2+8\beta_*(t-\tau)}\right] \times \\ \times \exp\left[-k_0(z + k_0\beta_*(t-\tau))\right] d\tau. \tag{1.10}$$

A probing beam of small power the wavelength of which λ is selected in the domain of maximal transparency of the magnetic fluid (for most magnetic fluids the maximum of light transmission lies in the region $\lambda = 0.76\mu m$ [3])

is used for the determination of the value of thermoelastic oscillations in the investigated medium. In the present paper transverse geometry of interaction of exciting and probing beams has been considered. The deflection angle of the probing beam based on (1.10) is defined from the relation [6]

$$\Phi(x, z, t) = \frac{1}{n}\frac{dn}{dT}\int_{y} \frac{\partial T(x, y, z, t)}{\partial x}\, dy, \tag{1.11}$$

where dn/dT is the temperature gradient of the refractive indexes (for fluids dn/dT usually has the order $10^{-4\circ}C^{-1}$). Substituting the expression (1.10) in (1.11) and fulfilling integration along the axis OY, one can define the value of the deflection angle [9,10]:

$$\Phi = \frac{1}{n}\frac{dn}{dT}\frac{k_0}{k_*} x\sqrt{2\pi}\int_0^t \frac{f(\tau)}{(a^2 + 8\beta_*(t-\tau))^{3/2}} \exp\left[-\frac{2x^2}{a^2 + 8\beta_*(t-\tau)}\right]$$
$$\times \exp[-k_0(z + k_0\beta_*(t-\tau))]\, d\tau. \tag{1.12}$$

The derived expressions (1.10), (1.12) are sufficiently awkward and their integration in analytical form is rather complicated. Therefore in our subsequent work let us make use of numerical integration method [11] and analyze the dependence of deflection angles value on dissipation properties of magnetic fluid for the cases of continuous and pulse excitation of the investigated ferrocolloid.

2. PHOTODEFLECTION SPECTROSCOPY OF MAGNETIC FLUIDS WITH CONTINUOUS EXCITATION.

Let the intensity of radiation exciting magnetic fluid change in accordance with the sinusoidal law with the frequency of the amplitude modulation Ω. Let us also assume that the radiation is modulated with the frequency $\omega \gg \Omega$ on linear polarizations along and across the field which magnetizes the fluid [12]. In this case the function $f(t)$ in the equation (1.2) will assume the form:

$$f(t) = (1 + \cos(\omega t))(1 + \cos(\Omega t)). \tag{2.1}$$

While using polarized modulation it is convenient to consider the expression for the difference of volume dissipation of energy of orthogonal components of the light beam instead of the equation (1.1)

$$\Delta Q(\mathbf{r}, t) = Q_{\parallel} - Q_{\perp} = k_r I(\mathbf{r}, t) \exp(-k_0 z), \tag{2.2}$$

where k_r is the value of relative linear dichroism ($k_r = (k_{\parallel} - k_{\perp})/k_0$, $k_{\parallel}$, $k_{\perp}$ are the coefficients of light absorption, polarized along and across the vector of the magnetic field intensity), defined for transparent carrier medium due to [2] by the relation

$$k_r = \frac{3\,Im(\alpha_{\parallel} - \alpha_{\perp})}{Im(\alpha_{\parallel} + 2\alpha_{\perp})} a' L_2(\zeta), \tag{2.3}$$

here $\alpha_{\parallel,\perp}$ are components of the tensor of the polarizability of the particle, $L_2 = 1 - 3L/\zeta$, $L = \coth\zeta - \zeta^{-1}$ is the Langevin function describing the balanced magnetization of the ensemble of the non-interacting ferroparticles, $\zeta = mH/kT$ is the Langevin argument, m is the magnetic moment of a particle, H is the intensity of the magnetic field, k is the Boltzmann constant, T is the temperature, $a' = 3/2(F'/F - 1/3)$, $F = \int \exp(\sigma x^2)\,dx$, $F' = \partial F/\partial\sigma$, σ is the parameter of the effective magnetic anisotropy of a ferrocolloid. For particles in the form of rotation ellipsoid [2]

$$\alpha_{\parallel,\perp} = \frac{\varepsilon_1(\varepsilon_2 - \varepsilon_1)}{4\pi((\varepsilon_2 - \varepsilon_1)n_{\parallel,\perp} + \varepsilon_1)}, \tag{2.4}$$

where ε_1 is the permittivity of carrier medium, $\varepsilon_2 = \varepsilon_2' + i\varepsilon_2''$ is the complex permittivity of the ferroparticle, and $n_{\parallel,\perp}$ are defined by the expression

$$n_{\parallel} = \frac{(1 - e^2)}{2e^2}\left[\ln\left(\frac{1+e}{1-e}\right) - 2e\right], \qquad n_{\parallel} + 2n_{\perp} = 1, \tag{2.5}$$

$e = 1 - (b/a)^2$, $\tau = b/a$ is the ellipticity of the particle form.

The dissipation difference of energy of orthogonal polarizations (2.2), as follows from (2.3)–(2.5) shows a strong dependence on the form of the particle. When the particle tends to the spherical shape, when $\tau \to 1$, $e \to 0$, the value ΔQ also approximates zero the faster the less the value of the intensity of the external magnetic field (curve 1, fig.1). Together with the increase of the intensity of the external magnetic field H the value of the difference of the dissipated energy tends to saturation (fig.2) which is connected with the reorientation of all the particles of the fluid in the direction of the field.

On the graph of dependence $\Delta Q = f(\tau)$ for small values H maxima take place (curves 1,2, fig.1) which disappear with the increase of the magnetic field. This can be probably accounted for by incomplete orientation of ferroparticles at field values H below H_{st}. The maxima of the curved lines 1,2 on fig.1 correspond to the limit value of the dichroism at the complete orientation of all the particles of the magnetic fluid in the direction of the vector H. And the maximum of the energy dissipation difference is obtained depending on the value of magnetizing field at different values of anisotropy of particle form. The smaller τ, i.e. the nearer particles are to needle shape, the faster occurs their reorientation in the direction of magnetizing field and subsequent saturation of value ΔQ.

The calculations show that the temperature distribution in magnetic fluid has symmetric shape with the maximum in the geometric center of the exciting beam (fig.3). Deflection angle of a probing beam greatly depends on the geometry of reading out and kinetics of photoacoustic transformation in the magnetic fluid. Within the limits of the orientation model of the magnetic colloid [2] small particles of ferromagnets are of the same domain, the magnetic moment of a separate particle is large enough ($m_0 \sim 2 \cdot 10^{-16}\, Gs \cdot cm^3$), as a consequence the value of paramagnetic susceptibility increases. The calculations show that the value of the probing beam deflection angles in such fluids will reach a few angular seconds. Therefore it is convenient to carry out measurements when the value of the magnetic field is large and the difference of energy dissipation is close to saturation. The value of the deflection angle in this case will also be maximal (fig.4). The changes of the frequency of the amplitude modulation of the exciting laser beam leads to the traditional dependencies in photoacoustic spectroscopy [13,14]. With the increase of Ω there occurs decrease of the amplitude of the signal, which is explained by the inability of the medium to respond to the quick changes because of the thermal sluggishness.

3. PHOTODEFLECTION SPECTROSCOPY OF MAGNETIC FLUIDS WITH PULSE EXCITATION.

The use of the method of the Green functions for the solution of the equation of heat conduction (1.3) allows to consider both continuous and pulse exciting radiation.

In the present section two types of functions modulating the source of exciting radiation are considered:

$$1)\quad f(t) = I_0;\ 0 < t < T_i \qquad f(t) = 0;\quad t > T_i. \tag{3.1}$$

This case corresponds to the square pulse of T_i duration.

$$2)\quad f(t) = I_0 \exp\left(-\frac{t^2}{2t_i^2}\right). \tag{3.2}$$

This type of modulating function describes the pulse of radiation, the intensity of which decreases according to the Gaussian law. The parameter t_i characterizes halfwidth of the pulse.

On the basis of the expressions (1.10), (1.12) there has been carried out the calculation of the angular value of the probe beam deflection in the magnetic fluid as a function of the time of action of the exciting radiation, the duration of pulses and the frequency of their sequence. The following case has been considered: the exciting radiation was linear polarized, the oscillations of the vector **E** are parallel and orthogonal to the vector of the external magnetic field strength **H** acting on the fluid. Besides there has been considered the dependence of the deflection angle on the radius of the exciting beam.

From fig.5 it follows that the frequency of the pulse sequence has a great influence on the magnitude of angular deflection. The signal increases with the decreasing of the relative pulse duration, which can be explained by the thermal sluggishness of the medium. Yet it must be taken into consideration the local processes may occur with great heating. Their analysis can be complicated. For instance, the boiling temperature of the magnetic fluid consisting of magnetite $FeO{\cdot}Fe_2O_3$ particles dispersed in water is $\sim 26\,^{\circ}C$ in the considered range of volume concentrations [3]. The boiling temperature decreases with the increase of the volume concentration of the solid phase. The calculations show that the magnetic fluid adjoining the zone of the geometric center of the beam reaches the boiling temperature within the time $t = 0.8\,s$ with the power of laser radiation $P = 2W$.

Rather of interest is the case when the magnetic fluid is excited by two

short pulses following within a considerable period of time and radiation in the first pulse is parallel polarized while in the second one is orthogonal polarized to the external magnetic field H. As follows from (1.10), (1.12) experimental measurement of difference values of the deflection angles of the probe beam allows to define the value of relative linear dichroism of a magnetic ferrocolloid

$$k_r = \Delta\Phi(x, z, t)\left(-\frac{\sqrt{2\pi}}{nk_*}\frac{dn}{dT}\int_0^t \frac{f(\tau)}{(a^2+8\beta_*(t-\tau))^{3/2}}\right)^{-1} \times$$
$$\left(\exp\left[-\frac{2z^2}{a^2+8\beta_*(t-\tau)}\right]\exp[-k_0(z+k_0\beta_*(t-\tau))]d\tau\right)^{-1}. \qquad (3.3)$$

Pulses generated by real devices are often described by the Gaussian law (3.2). For instance, pulses radiated by the $He-Ne$–laser with modulated Q-factor have Gaussian time distribution. The dependence of deflection angular value Φ on the time of excitation with different halfwidth of such pulses is shown in fig.6,7. It is necessary to note, that according to our calculations the angular value of deflection increases with modulation of exciting radiation by Gaussian pulses compared to the case when exciting radiation is modulated by square pulses of the same duration. This can be seen while comparing fig.5 and fig.7. Thus, even insignificant change of the form of the pulse front from rectangular contributes essentially to the value of the energy absorbed in the magnetic fluid.

As it was mentioned above, the analytic integration of the expression (1.12) is difficult, therefore we shall also use computational methods for the investigation of the influence of the exciting beam radius a on the deflection angle. Fig.8 shows the dependence of the angular deflection of the probe beam on the radius of the beam exciting the magnetic fluid. It is seen from fig.8, that the maximum of the angle Φ corresponds to the value $a \sim 2z$. Thus it is necessary to carry out measurements in the vicinity of the point with the reduced coordinate $z/a = 1/2$, in order to achieve the maximal angle of deflection with the given parameter a.

CONCLUSION.

Thus in the paper peculiarities of laser photodeflection spectroscopy method have been analyzed as applied to the magnetic fluids at transversal geometry of interaction. The possibility of defining the value of relative linear dichroism of magnetic fluid by photodeflection method has been shown. From the presented theoretical calculations it follows that it is more convenient to use the continuous modulation of exciting laser radiation for the investigation of dissipative characteristics of diluted magnetic fluids (volume concentration of the solid phase $c \leq 10^{-5}$), as the deflection angles of the probe beam increase in this case compared with the case of pulse modulation. In the case of more concentrated magnetic fluids it is preferable to use the pulse method of modulation, for it allows to avoid local overheat of the investigated medium during the increase of the power of exciting radiation.

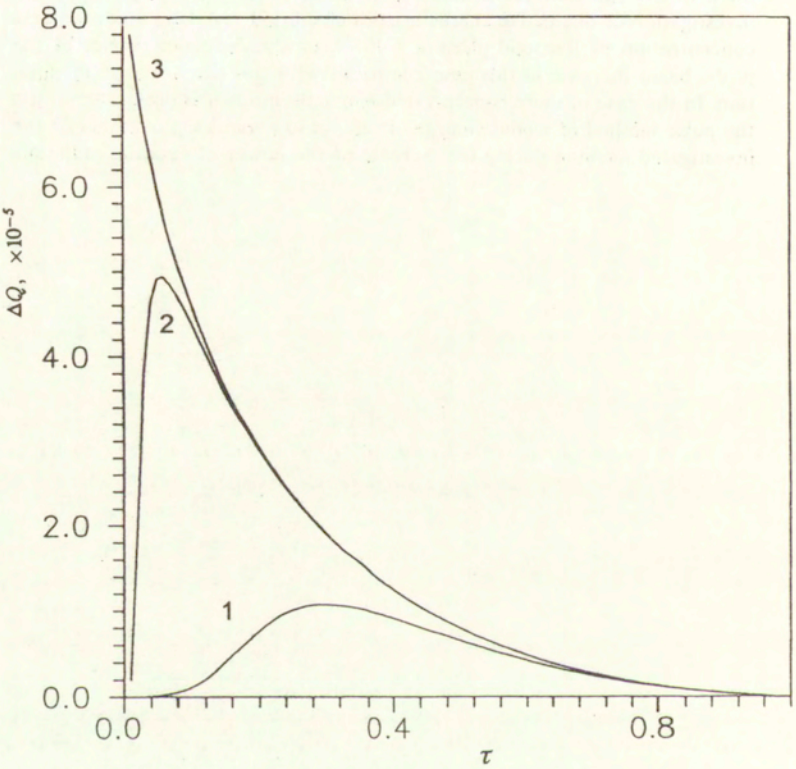

Fig.1 Dependence of the difference of energy dissipation ΔQ on the ellipticity of the particle form with the different external magnetic field H: $1 - -H = 10\,A/m$, $2 - -H = 100\,A/m$, $3 - -H = 100\,kA/m$.

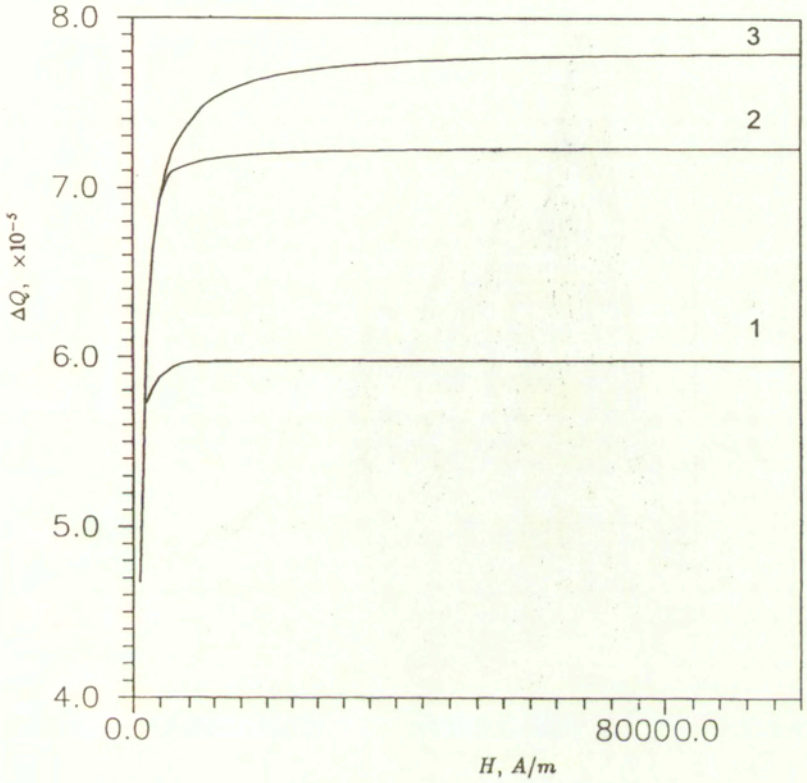

Fig.2 Dependence of the difference of energy dissipation ΔQ on the magnitude of the external magnetic field **H**: $1 - -\tau = 0.1$, $2 - -\tau = 0.05$, $3 - -\tau = 0.01$.

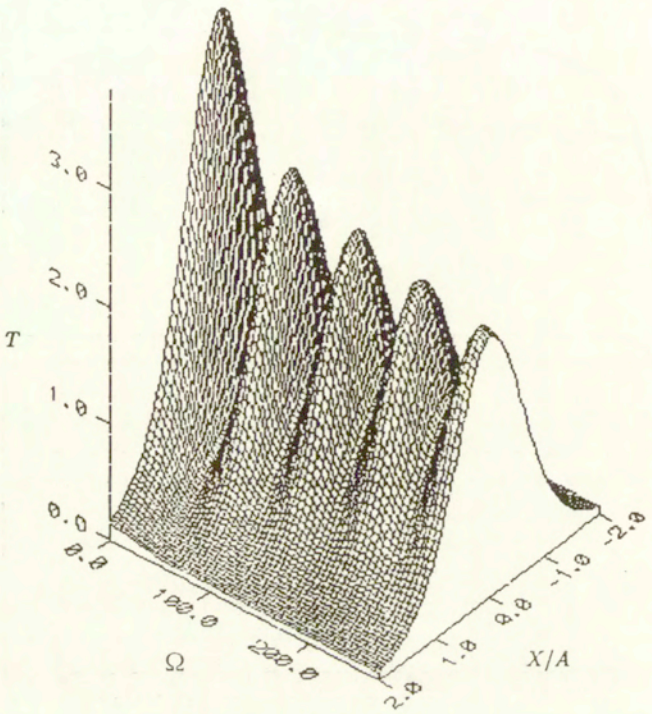

Fig.3 Dependence of the temperature T on the reduced coordinate X/A and the frequency of amplitude modulations of exciting radiation Ω.

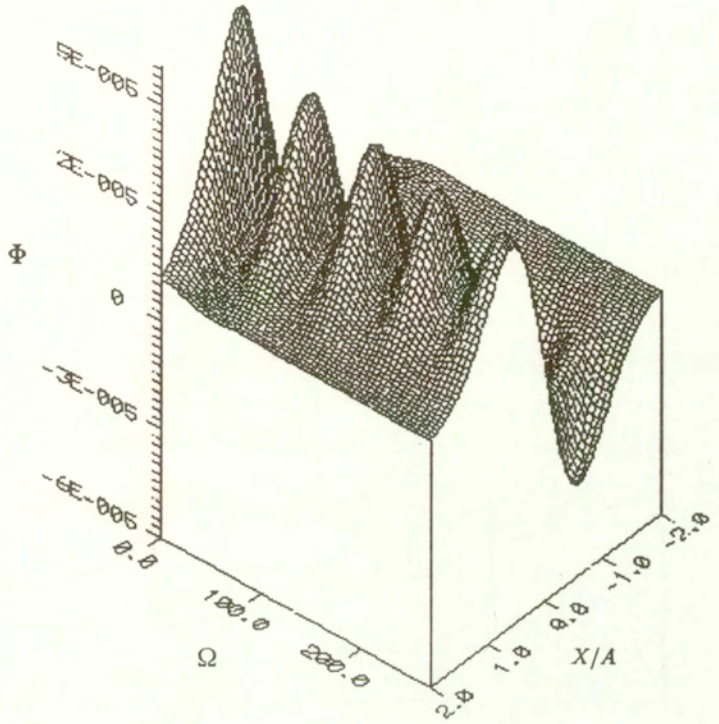

Fig.4 Dependence of the deflection angle Φ on the reduced coordinate X/A and the frequency of amplitude modulations of exciting radiation Ω.

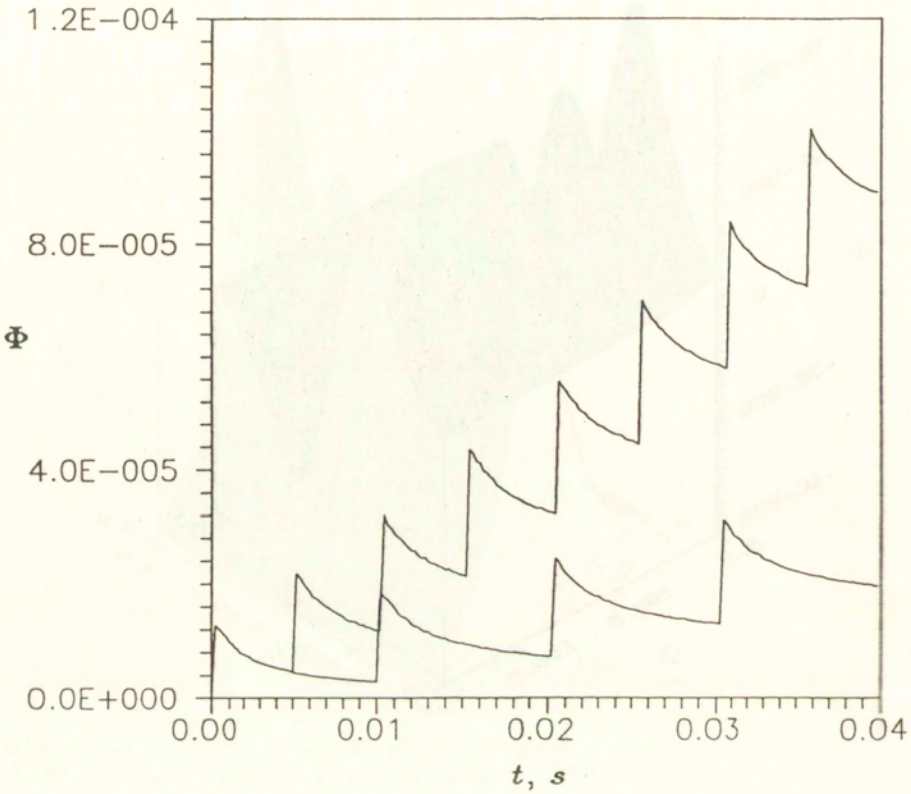

Fig.5 Dependence of the deflection angle Φ on the time of interaction with modulation of exciting radiation by square pulses of the duration $T_i = 10^{-4}$.

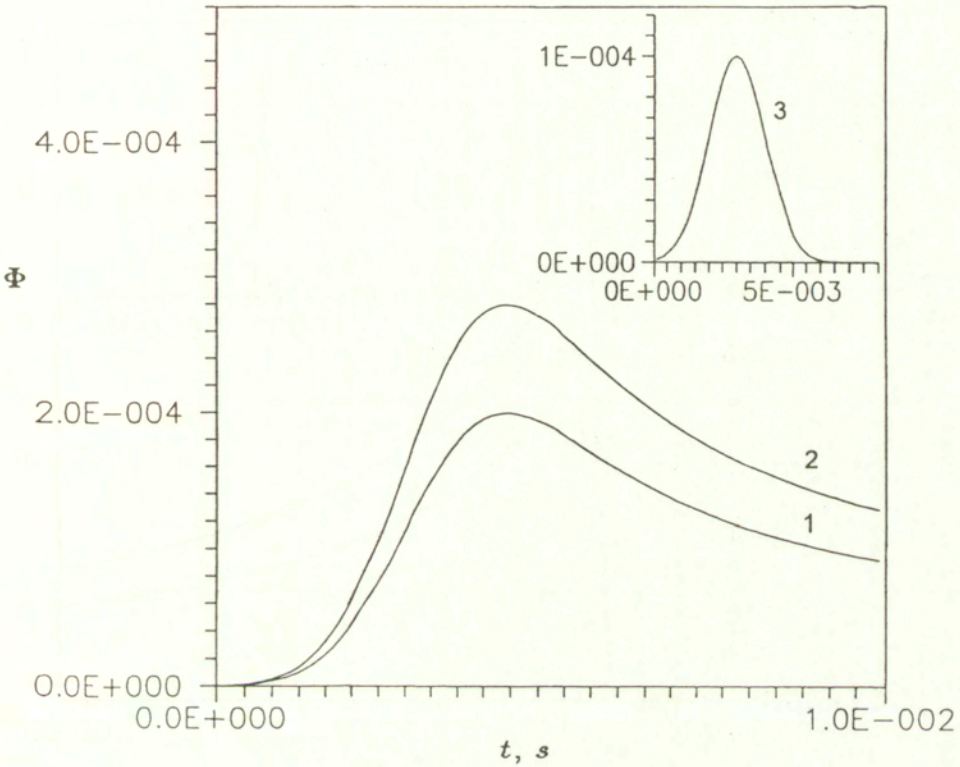

Fig.6 Dependence of the deflection angle Φ on the time of interaction with modulation of exciting radiation by pulses of Gaussian form: 1 – polarization along the magnetic field, 2 – polarization across the magnetic field, 3 – form of the pulse.

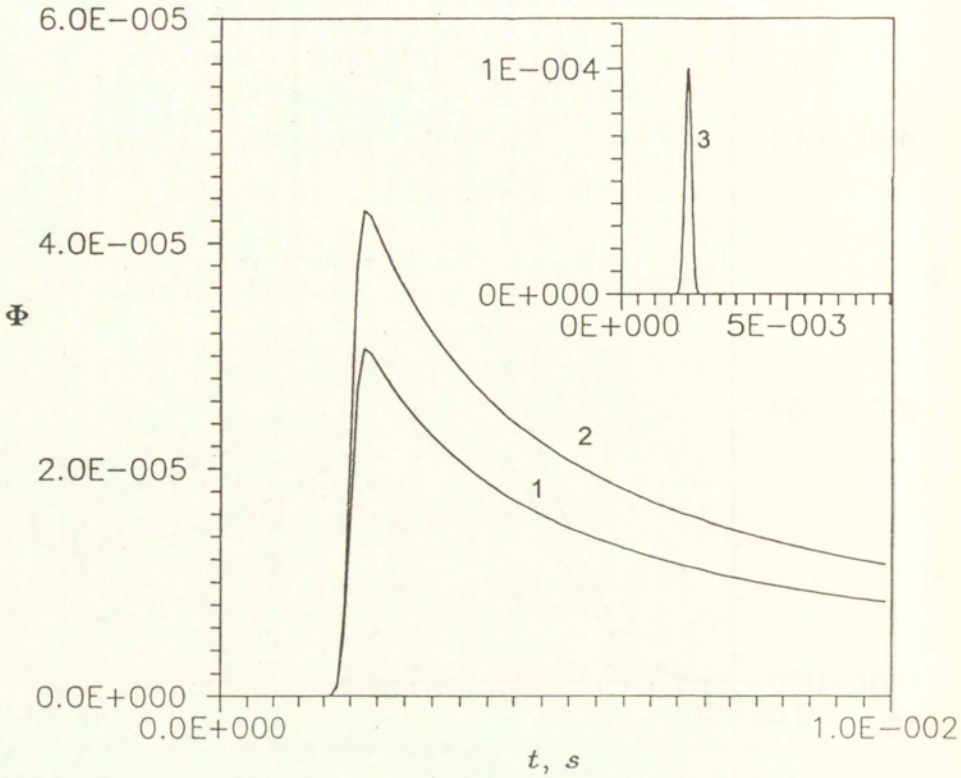

Fig.7 Dependence of the deflection angle Φ on the time of interaction with modulation of exciting radiation by pulses of Gaussian form: 1 – polarization along the magnetic field, 2 – polarization across the magnetic field, 3 – form of the pulse.

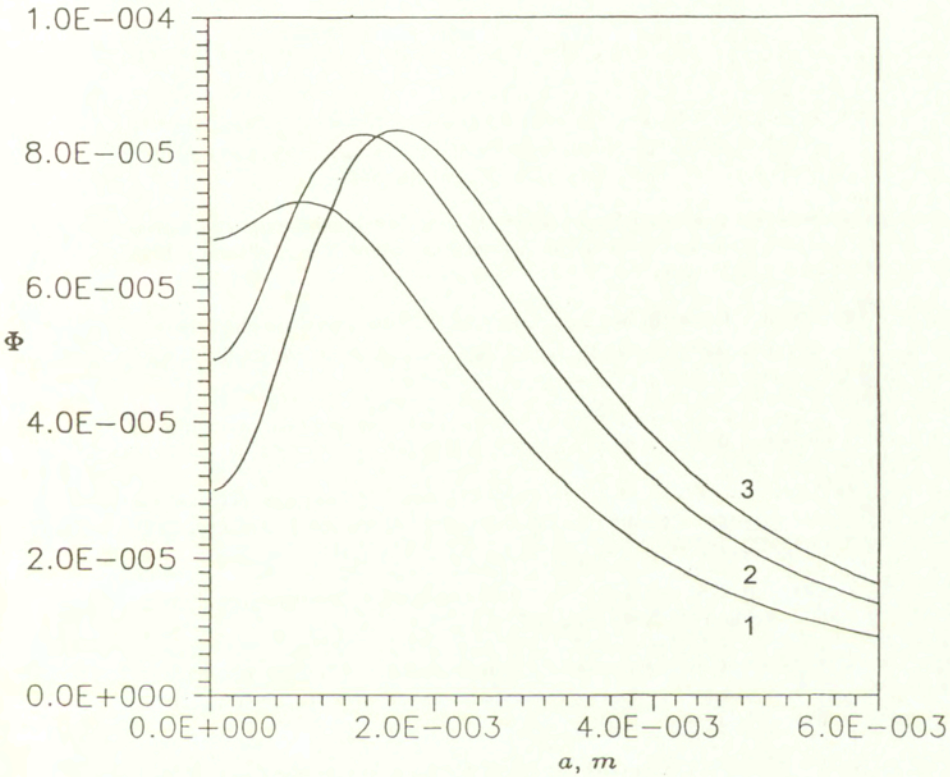

Fig.8 Dependence of the deflection angle Φ on the radius of the exciting beam: $1 - -x = 0.0005\,m$, $2 - -x = 0.0008\,m$, $3 - -x = 0.001\,m$.

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