

X-ray Diffraction Study of Gadolinium Stearate Langmuir–Blodgett Films

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Abstract—The comparative structural studies of gadolinium stearate Langmuir–Blodgett films prepared with the use of two different subphases (aqueous solutions of gadolinium chloride and gadolinium acetate) have been performed by the methods of X-ray diffractometry. The films were applied onto single-crystal silicon substrates coated with a native-oxide layer either with the use of buffer molecular stearic-acid layers or without such layers. It was established that the films obtained with the use of gadolinium acetate and the preliminarily formed buffer layers are, in fact, single-phase *Y*-type films with highly ordered molecular structure, and the thickness of the bimolecular layer $d = (51.3 \pm 0.5)$ Å. © 2002 MAIK “Nauka/Interperiodica”.

INTRODUCTION

Langmuir–Blodgett (LB) films of fatty acids are highly ordered two-dimensional layered structures with periods of the order of several nanometers [1]. Their physicochemical properties depend, to a large extent, on the metal cations incorporated into the molecular matrix. Langmuir–Blodgett films are very promising materials for molecular electronics, nanotechnology, and various quantum devices [2–5], as well as for the modeling of two-dimensional physical systems, because the material of these films can be considered as a certain layer matrix. Metal ions incorporated into Langmuir–Blodgett films form two-dimensional arrays distributed with a certain spatial periodicity. The incorporation into the films of metal cations possessing intrinsic magnetic moments make them similar to two-dimensional magnetic films. One of the first studies along these lines [6–9] was performed on manganese stearate $[\text{Mn}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2]$ Langmuir–Blodgett films. It was established that manganese stearate could be deposited onto the substrate either as an individual monolayer or as a multilayer film with a period of ~ 50 Å. It was also shown that the magnetic moments of manganese ions are ordered as in antiferromagnetic compounds and that the magnetic phase transition temperature equals ~ 10 K.

Possible magnetic ordering at high temperatures in gadolinium stearate films was indicated in [10, 11].

Magnetic ordering in Langmuir–Blodgett films containing gadolinium ions occurs up to a temperature of ~ 500 K [12]. Gadolinium is a ferromagnetic with a Curie temperature ~ 294 K and a hexagonal close-packed lattice $[\text{Mg}(\text{A}3)D_{6h}^4 - P6_3/mmc]$ with the unit-cell parameters $a = 3.636$ Å and $c = 5.783$ Å. The electronic structure of a gadolinium atom is such that $4f$ -electrons are inside the filled $5p$ -shell and the wave functions of the $4f$ -levels of the nearest neighboring atoms from different coordination spheres do not overlap. As a result, the indirect exchange interactions in metal Gd occur via conduction electrons [13, 14]. The local intrinsic magnetic moment of Gd atoms is created by seven $4f$ -electrons and equals $7\mu_B$. The wave functions of the $5d$ - and $6s$ -electrons of the neighboring atoms considerably overlap and provide chemical bonding between these atoms.

Along with thin epitaxial metal films and surface layers of various magnetics, the LB films can be considered as a promising model for studying two-dimensional magnetism. However, it should be remembered that the preparation of quasi-two-dimensional epitaxial films is associated with considerable technological difficulties in the preparation of substrates with atomically pure surfaces and the growth of perfect thin films and atomic layers. It should also be indicated that the methodological aspect of the preparation of a two-dimensional magnet based on a gadolinium-containing LB

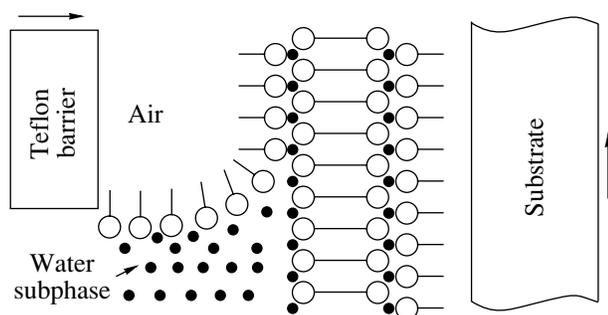


Fig. 1. Scheme of preparing gadolinium stearate LB films and their molecular structure.

film depends, first and foremost, on the technology of its growth, the choice of the organic matrix, and the incorporation of gadolinium atoms into the film [15]. All these problems are the subject of the present study.

Below, we consider the results of X-ray diffraction studies of the structural characteristics of gadolinium stearate LB films formed on single-crystal silicon substrates coated with a layer of native oxide obtained with the use of two different subphases—aqueous solutions of gadolinium chloride and gadolinium acetate.

EXPERIMENTAL

Preparation of Langmuir–Blodgett Films

We used stearic acid $C_{18}H_{36}O_2$ (Serva, Germany) and gadolinium chloride and gadolinium acetate (Aldrich, USA). Water was deionized with the aid of a MilliQ system for water purification (Millipore, USA). Langmuir monolayers were transferred onto solid substrates and were studied on an automated setup described elsewhere [16]. In order to obtain a stearic-acid monolayer the stearic acid (SA) solution in 4×10^{-4} M chloroform was spread onto a clean surface of the subphase. Ten minutes later (upon the evaporation of the solvent and the attainment of the adsorption equilibrium), the monolayer was compressed at a rate of $3 \text{ \AA}^2/(\text{SA molecule}) \times \text{min}$ with a simultaneous record of the compression isotherm. The monolayer was transferred from the

Table 1. Structural parameters of various phases of stearic acid

Phase	Parameters, \AA	Card JCPDS
<i>B</i> -monoclinic	$a = 5.710, b = 7.390,$ $c = 50.70, \beta = 119.9^\circ$	9-622
<i>C</i> -monoclinic	$a = 9.378, b = 7.390,$ $c = 39.960, \beta = 94.81^\circ$	38-1923
<i>E</i> -orthorhombic	$a = 15.00, b = 22.50,$ $c = 22.50$	8-594
<i>F</i> -orthorhombic	$a = 16.50, b = 24.70,$ $c = 24.700$	8-668

surface of the aqueous phase onto a solid substrate [a polished (100)Si surface] by the method of vertical lifting of the substrate under a surface pressure of 30 mN/m at a temperature of 20°C. The velocity of substrate immersion was 5 mm/min. The concentration of gadolinium salts [$GdCl_3$ and $Gd(CH_3COO)_3$] was 10^{-4} M at pH 5.5. Figure 1 illustrates the formation of gadolinium stearate Langmuir–Blodgett films onto the substrates and shows their possible three-dimensional structure.

X-ray Diffraction Measurements

The integral diffraction patterns ($\theta/2\theta$ scan) were recorded on a multicrystal X-ray spectrometer based on the Rigaku D/max-RC diffractometer with a 12 kW X-ray radiation source with a rotating anode. We used the $K_{\alpha 1}$ -line of a copper-anode radiation. The primary radiation was monochromatized by a tunable double-reflection silicon crystal–monochromator. Depending on the angular resolution required, different single- and triple-reflection silicon crystal analyzers were used. Weak signals were recorded according to the classical scheme with the use of the pyrolytic graphite crystal (with an angular resolution of $\leq 0.1^\circ$).

RESULTS AND DISCUSSION

The surface-active substance forming a Langmuir monolayer on the aqueous-phase surface was stearic acid because of the highly ordered and compact arrangement of its carboxyl groups in the monolayer. According to the X-ray diffraction data for powder crystals, the solid phase of this compound can exist in four polymorphous modifications, *B*, *C*, *E*, and *F*, with different spatial orientations of C–H bonds with respect to the molecule axis (Table 1).

Only the *B* and *C* phases are present in multilayer stearate LB films, in which the pairs of molecules are aligned to form bimolecular layers. The length of these dimers depends not only on the tilt of the molecules and their mutual arrangement, but also on the packings of atoms (especially carbons) in the tails of methyl groups. Unlike the situation in single crystals, SA molecules in LB films form an independent triclinic *A* phase with the thickness of the bimolecular layer equal to $(46.1 \pm 0.5) \text{ \AA}$ [17, 18]. The space group of the packing of SA molecules in the films was determined from the transmission electron diffraction patterns. The spot-type electron diffraction patterns showed that the *A* phase is either monoclinic or orthorhombic with the unit-cell parameters $a = 5.0 \text{ \AA}$ and $b = 7.5 \text{ \AA}$ [19, 20]. In actual fact, LB films consist of different mixtures of the *A* and *C* or the *B* and *C* phases or of all three phases simultaneously, which, no doubt, changes the period of the layered structure of the film and provides its local variations. This should always be kept in mind while interpreting the X-ray diffractometric data.

The characteristic diffraction pattern from the 11-layer LB films of the stearic acid ($\theta/2\theta$ scan) is shown in Fig. 2a. The thicknesses of the bimolecular layer or the periods of the films measured from diffraction patterns range within 46–48 Å. It should be emphasized that the experimental values considerably differ from the known powder diffractometric data for the *B* phase but are close to the measured period of layer alternation (46.1 ± 0.5 Å) in the LB films consisting of the molecules of the *A* phase [17]. Thus, it can be assumed that the stearic-acid films obtained in our experiments are formed mainly by the molecules of the *A* phase. However, the question of whether the films really consist of only one phase or not is still open.

It is interesting to compare the structural perfection of the films prepared by the transfer of SA monolayers from the surface of the aqueous solutions of various gadolinium salts onto substrates. We did experiments on gadolinium chloride GdCl_3 and gadolinium acetate $[\text{Gd}(\text{CH}_3\text{-COO})_3]$ (the salts of the acetic acid). It turned out that the structure of the LB films obtained at the same pH and the gadolinium salt concentration in the aqueous subphase depended on the nature of the acidic residue of the salt. The diffraction patterns from LB films obtained with the use of a gadolinium chloride solution ($\theta/2\theta$ scan) clearly show only one considerably broadened peak (the second one) with the integrated halfwidth $W_R = 0.794^\circ$ (Fig. 2b), whereas the other narrow peaks characterized by $W_R = 0.2^\circ$, including the first one, are very weak. X-ray diffraction from thin LB films is described by the kinematical theory of scattering. Therefore, the diffraction pattern can be considered as two overlapped independent series of reflections due to two independent phases having different molecular structures. It is also necessary to take into account the superposition of individual reflections, which makes the interpretation of the diffraction pattern even more difficult.

The intensities at the maxima (I) and the integrated intensities ($I_i = kN_i$), the halfwidths (W_R) of the reflection curves, and the layer periods (d) calculated from the experimental values of the Bragg angles are indicated in Table 2 (series 1). These data show that the gadolinium stearate LB films consists of two phases having different periods, $d_1 = 25.2$ or 50.4 Å and $d_2 = 47.6$ Å. However, since the first reflection is very weak, the structure of such films can be described by two models. In the first model, the reflection formed at the Bragg angle $2\theta = 3.5^\circ$ is assumed to be the 001 reflection and, therefore, the film should consist of the *E* or *F* phase and not the *A* phase, because almost the whole integrated intensity is concentrated in this reflection. In the second model, this reflection is indexed like the second, 002, reflection of the *A* phase, but the first peak due to this phase is practically invisible on the diffraction pattern because of pronounced diffuse scattering from the molecular distortions of the film. The second phase

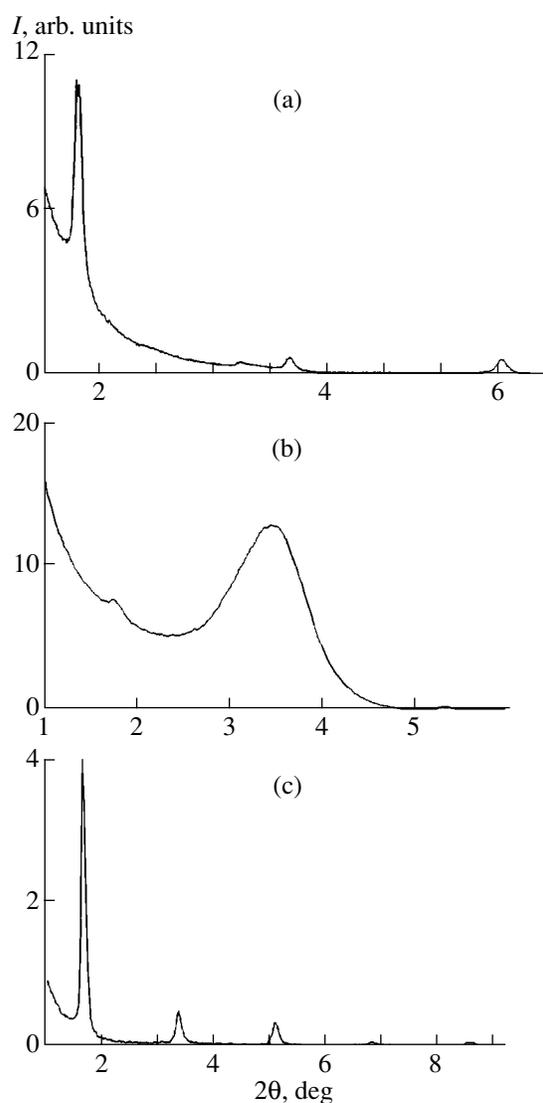


Fig. 2. Diffraction pattern ($\theta/2\theta$ scan) of LB films of (a) the stearic acid (five bilayers, the period $d = 47.6 \pm 0.5$ Å), (b) gadolinium stearate on the polished silicon substrates coated with a layer of native oxide obtained with the use of an aqueous gadolinium chloride solution (the film thickness is up to 20 bilayers, pH 5.5), and (c) gadolinium stearate on the polished silicon substrates coated with a layer of native oxide obtained with the use of an aqueous gadolinium acetate solution (the film thickness is 80 bilayers, pH 5.5).

observed most probably corresponds to the stearic acid with the bimolecular-layer thickness $d_2 = 47.6$ Å.

The integrated intensities (I_i) show that the fraction of the second phase is insignificant (about 0.7%). The second phase is more probable and, therefore, we assume that the LB films consist mainly of molecules of the *A* phase.

The reflection broadening (W_R) is associated with the finite dimensions of the coherent-scattering region, $l = \lambda/(W_R \cos \theta)$. This corresponds to $l_1 = 110$ Å for the

Table 2. Results of X-ray diffraction study of Longmuir–Blodgett films

Sample series	<i>hkl</i>	<i>I</i> , pulse/s	<i>N_i</i> , pulse	<i>W_R</i> , deg	2θ, deg	Interlayer period <i>d</i> , Å
1	001	4064	–	–	2.86	42.9
	002	7526	162311	0.79	3.50	50.4
	003	75	687	0.21	5.62	47.1
	004	25	158	0.17	7.42	47.6
	005	30	309	0.22	9.20	48.1
2	001	3921	25558	0.10	1.69	52.5
	002	509	4417	0.11	3.40	52.2
	003	284	2899	0.13	5.11	51.7
	004	58	738	0.15	6.85	51.8
	005	50	687	0.20	8.56	51.6
3	001	464	24561	0.55	1.73	51.1
	002	324	9728	0.19	3.74	47.2
	003	2144	61198	0.19	5.46	48.5
	004	729	19498	0.18	7.23	48.9
	005	702	18288	0.19	9.00	49.1
	006	122	1938	0.17	10.79	49.2
	007	101	2461	0.18	12.58	49.2
4	001	21115	382444	0.16	1.80	49.1
	002	1897	31011	0.19	3.62	49.2
	003	1113	23559	0.19	5.37	49.6
	004	153	3148	0.18	7.18	49.5
	005	159	3083	0.20	8.94	49.0
	006	28	446	0.10	10.73	49.4
	007	33	3031	0.19	12.30	49.4

first phase, and, according to the data for the (003), (004), and (005) reflections, to $l_2 = 420$ Å for the second phase. It is interesting that the experimental l_1 value equals double the period of the film, $2d_1 = 101$ Å, whereas the l_2 value is close to the film thickness (500 Å). The coherent-scattering regions for LB films are the regions with characteristic molecular structures. Therefore, the molecular structure of the LB films obtained with the use of the aqueous GdCl₃ solution as a subphase is represented by the following model. Gadolinium cations interacting with the stearic-acid molecules of the film form the complexes and, thus, bind two molecular bilayers, thus forming stable “chains” of SA molecules. In this case, the chain consists of four SA molecules, e.g., SA–SA–Gd–SA–SA. In the film bulk, these chains are arranged randomly and form a characteristic “texture.” Between the regions of phase 1, one can also encounter the regions of phase 2—long chains of stearic acid molecules which have not reacted with gadolinium cations (SA–SA–SA–SA...). Thus, the results obtained indicate that the use of gadolinium chloride as a source of gadolinium ions in the aqueous phase under the conditions of our experiments (pH 5.5,

gadolinium concentration 10^{-4} M) does not lead to the formation of perfect gadolinium stearate LB films. This can be explained by the complicated processes of formation of complexes by gadolinium cations on the monolayer surface, including the interaction with hydroxide and chloride ions, and also the specific mechanical properties of the monolayer and the interactions occurring during the monolayer transfer onto the substrate and the formation of the multilayered structure of the LB film. A similar dependence was also observed for cadmium stearate films [4].

The diffraction pattern from the films obtained with the use of the gadolinium acetate aqueous solution as a subphase is quite different. Figure 2c shows the typical X-ray diffraction patterns ($\theta/2\theta$ scan) from a thick (80 bilayers) gadolinium stearate film deposited onto the polished silicon substrate from the surface of the aqueous subphase by the method of vertical immersion of the substrate.

In the angular range $2\theta = 1^\circ$ – 10° , one can clearly distinguish narrow Bragg reflections of various orders. The characteristic feature of such diffraction patterns is the occurrence of the Bragg diffraction only in the angular range whose values are higher than the critical

angle (θ_{cr}) against the background of the X-ray specular reflection from the substrate and the successive decrease in the peak intensities of the diffracted beams with an almost constant width of Bragg reflections. The number of the recorded peaks is fully determined by the intensity of the primary X-ray beam.

The intensities (I) and (I_i), the halfwidths (W_R), and the layer periods (d) calculated from the Bragg angles (2θ) are indicated in Table 2 (series 2). The average value of the period of multilayer films determined from different values of the Bragg angles equals $d = (51.30 \pm 0.5) \text{ \AA}$.

It should be indicated that the X-ray diffraction patterns were measured at a high source power (6–8 kW) at an angular resolution of $\approx 0.1^\circ$ insufficient for studying gadolinium stearate LB films. The halfwidths and the maximum reflection intensities are also considerably affected by the apparatus function.

However, the incorporation of heavy gadolinium ions with a radius of 1.78 \AA into the layered stearic acid matrix consisting of light H, C, and O atoms with the covalent radii $R_H = 0.30$, $R_C = 0.77$, and $R_O = 0.74 \text{ \AA}$, respectively [21], can give rise to pronounced deformations and distortions of the matrix structure and its fragmentation, i.e., formation of regions similar to domains in the bulk ferromagnetics. Therefore, the Bragg diffraction in LB films can be accompanied by diffuse scattering from these individual structural inhomogeneities. The study of such fine structural problems requires qualitatively new X-ray experiments at a higher angular resolution ($\leq 0.01^\circ$).

The structural perfection of LB films considerably depends on the state of the substrate surface (its purity, relief, etc.). To avoid these effects, we used the molecular layers of the pure stearic acid as buffer layers. Figure 3 shows the diffraction patterns of gadolinium lead stearate LB film deposited directly onto a clean substrate (Fig. 3a) and onto a substrate coated with a buffer layer (Fig. 3b). The X-ray diffraction data obtained from these specimens are listed in Table 2 (series 3 and 4).

Comparing the diffraction patterns, we see that the relief of the substrate with the applied LB film considerably influences the film structure. The diffraction pattern in Fig. 3a shows not only a newly appeared broadened (001) reflection, but also shows that the dependence of the peak intensities on the reflection order is also changed. Unlike the diffraction pattern in Fig. 2a, we see that the first and not the third reflection that is broadened. The characteristic dimension of the coherent-scattering region determined from the peak halfwidth ($W = 0.55^\circ$) corresponds to the length of the molecular chain of gadolinium stearate, 160 \AA , which corresponds to the triple period $3d_{001} = 153 \text{ \AA}$. Therefore, the fragmentation of the LB film structure is accompanied by the formation of complexes in the form of molecular chains of the SA-SA-Gd-SA-SA-Gd-SA-SA-type. This is the shortest possible molecular chain. If there are ten layers, the chain length ranges from $3d$ to $10d$.

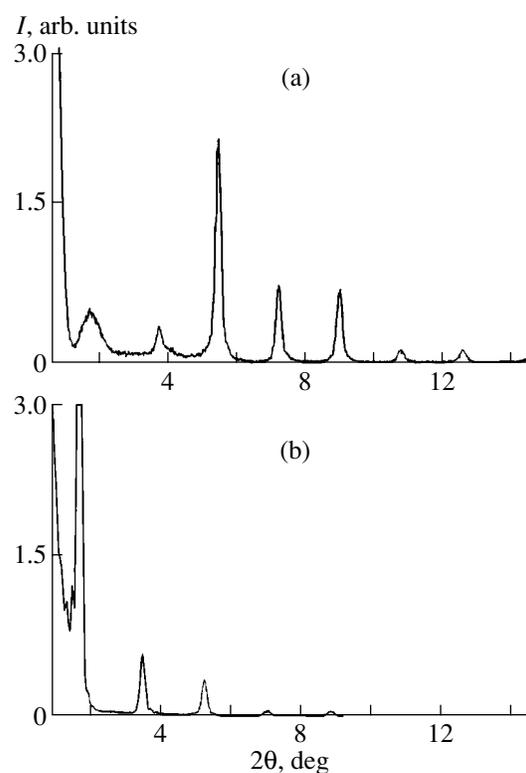


Fig. 3. Diffraction pattern ($\theta/2\theta$ scan) of a gadolinium stearate LB film (10 bilayers) on polished silicon substrates coated with layer of native oxide (a) without a buffer molecular layer of stearic acid and (b) with such a buffer layer. The thickness of the buffer layer equals three bilayers.

The molecular $3d$ -chains can form clusters possessing a certain short-range order, which can result in a considerable decrease in the peak intensity of the (001) reflection. These clusters may comprise up to 18% of the total volume. In a similar way, it is also possible to explain the anomalous changes in the intensities of other reflections on the diffraction pattern.

The stearic acid molecules located on the substrate surface of the buffer layer smoothen this surface and thus facilitate the formation of the regions with extended ordered chain structures built from gadolinium-stearate molecules during the film application. The halfwidths of all the reflections on the diffraction pattern (Fig. 3b) are almost equal, $W = 0.18^\circ$. This value corresponds to the dimension of the coherent-scattering region equal to 512 \AA or $l = 10d$. It follows from the diffraction data that in the LB films studied there are no molecular chains shorter than $l = 10d$. Therefore, the studies performed allow us to state that the gadolinium stearate LB films obtained from the subphase of the aqueous gadolinium-acetate solution onto the single-crystal silicon substrates consist of only one phase and have homogeneous composition and perfect structure. The average period of the layers determined from the differences of the Bragg angles is $d = (50.1 \pm 0.5) \text{ \AA}$.

Figure 4 shows X-ray specular reflection curves in the vicinity of the critical angles for a silicon substrate (curve 1) and gadolinium stearate LB films [series 3

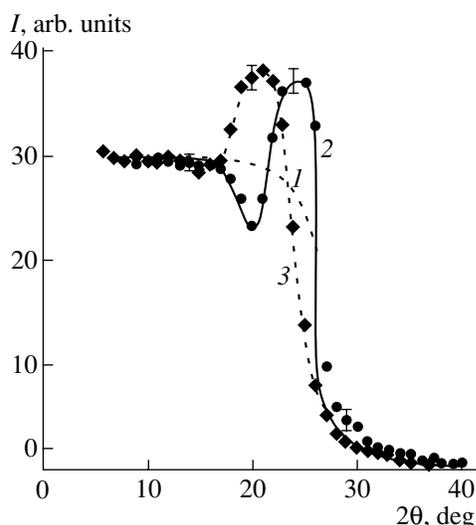


Fig. 4. X-ray specular reflection curves for (1) single-crystal silicon substrate and (2, 3) gadolinium stearate films (ten bilayers) (2) with a stearic acid buffer layer and (3) without a buffer layer.

and 4 (curves 2 and 3)]. For the single-crystal silicon substrate (curve 1), no specific features in X-ray specular reflection were revealed, and the angular dependences are described by the well-known Fresnel expressions [22] with the critical reflection angle $\theta_{cr} \sim 13' - 14'$. The application of an LB film onto the substrate results, on the one hand, in a slight decrease in the critical angle, and, on the other hand, in the dispersion form of the angular dependence of the reflection intensity, i.e., in the appearance of the corresponding minimum and maximum.

This X-ray scattering pattern can be explained on the basis of the following simple model [22]. Assuming that in the gadolinium stearate–silicon substrate system the refractive index of the film is less than that of the substrate, we can state that the incident X-ray beam (at the incidence angles exceeding the critical angle for the film) propagates in the film bulk, and, if the film is inhomogeneous, is scattered by various structural defects or electron-density inhomogeneities. The refracted waves are reflected by the substrate and emerge to the surface, where they interfere with the waves reflected from the film. In the vicinity of the critical angle, the phase of the reflected waves is changed by π [22, 23], and, therefore, the angular dependence of the X-ray specular reflection at the angles $\theta \sim \theta_{cr}$ acquires the dispersion form (curves 2 and 3).

One can evaluate the angle θ_{cr} for gadolinium stearate Langmuir–Blodgett films. The critical angle of the total external reflection of the X-ray radiation and the refractive index are determined by the material polarizability χ as follows: $\theta_{cr} = (|\chi_{r0}|)^{1/2}$, $n^2 = 1 - |\chi_{r0}|$, $\chi_0 = r^e (\lambda^2/\pi\Omega) \sum_j f_0^j$, where $|\chi_0|$ is the modulus of the real part of the Fourier coefficient of the crystal polarizabil-

ity, f_0 is the atomic scattering factor, $r^e = e^2/mc^2 = 2.8 \times 10^{-13}$ cm is the classical radius of an electron, Ω is the unit cell volume, and λ is the radiation wavelength.

For silicon crystals whose unit-cell volume $\Omega = 161 \text{ \AA}^3$ contains eight atoms, the critical angle at the wavelength $\lambda = 1.5405 \text{ \AA}$ equals $13.37'$ at $|\chi_{r0}| = 15.127 \times 10^{-6}$. The calculation of the Fourier coefficients of molecular-crystal polarizability involves certain difficulties. Their rigorous calculation should be made by the formula of the structure factor including the atomic coordinates in the molecule. However, this requires knowing the model of the packing of the atoms in the molecule, whose determination itself is a complicated problem of the X-ray diffraction analysis of organic materials. Therefore, we assume that the $|\chi_0|$ values for gadolinium stearate and the stearic-acid crystals differ only insignificantly. Then, one molecule of the A-phase occupies the volume with a base of $5.0 \times 7.5 = 37.5 \text{ \AA}^2$ and a height equal to a half-thickness of the bimolecular layer ($d/2$) of the film. In this case, the critical angle equals $\theta_{cr} = 6.84'$, i.e., has a value lower than the critical angle for silicon $\theta_{cr} = 13.37'$.

It should be indicated that interference can occur only in single-phase homogeneous LB films. Therefore, the films of series 4 prepared with the use of an aqueous gadolinium acetate solution as a subphase on a single-crystal silicon substrate coated with a buffer molecular layer satisfy this condition (curve 2 in Fig. 4). If LB films are inhomogeneous and have some “defect regions,” diffuse (small-angle) scattering takes place and suppresses the X-ray specular reflection (curve 3). In this case, interference is weakened and a peak with an anomalous intensity is formed in the vicinity of the critical angle of the film due to the “condensation” of diffuse scattering [24]. Measuring the angular range of nonspecular reflection, one can determine the linear dimensions of these inhomogeneities, $D \leq \lambda/2\Delta\theta_{cr} = 400 \text{ \AA}$. The defect structure is characteristic of LB films of series 3 obtained with the use of gadolinium acetate solution and single-crystal silicon substrate without a buffer molecular layer. The study of the nature of these defects is a separate problem. However, we assume that these defects can be certain complexes of gadolinium atoms formed at the interface between the bimolecular layers.

CONCLUSION

Our studies showed that gadolinium stearate LB films obtained with the use of aqueous solutions of gadolinium chloride and gadolinium acetate as subphases are characterized by different degrees of structural perfection. The films obtained with the use of the GdCl_3 solution consist of two phases, whose layers are disordered and bimolecular layers are considerably distorted. The films obtained with the use of gadolinium acetate and single crystal silicon substrates with buffer molecular layers are practically of single phase, are characterized by a high degree of perfection of molec-

ular structure, and can be used for creating two-dimensional magnets.

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