Observation of evanescent and standing x-ray waves in region of total external reflection from molecular Langmuir-Blodgett films

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The existence of an evanescent x-ray wave, which decays exponentially with distance into the film, and of a standing x-ray wave with a large and varying period has been demonstrated clearly in the region of total external reflection from a Langmuir-Blodgett film. The standing wave can be utilized to obtain structural information about multilayer organic systems.

Research on various 2D systems which might be used as elements for the artificial construction of multilayer structures and superlattices has attracted much research interest. Among these entities are molecular Langmuir-Blodgett films, which are synthesized, as we know, through a layer-by-layer crystallization on a solid substrate of molecular layers of amphiphilic molecules, which have a long tail (usually a hydrocarbon tail, with a length on the order of tens of angstroms) and a hydrophilic head (Ref. 1 for example). The multilayer structures built from such molecular layers are highly

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ordered systems in which layers of heavy metal atoms which are constituents of the molecules are separated from each other by hydrocarbon chains.

Systems of this sort are of more than purely physical interest. They are attracting attention because of practical reasons: Multilayer systems based on Langmuir-Blodgett films would be the building blocks of a future molecular electronics.

The practical use of such systems must of course be preceded by a comprehensive study of them. In particular, it is necessary to obtain detailed structural information. The x-ray diffraction methods which are widely used for this purpose, however, are incapable in their standard versions of studying thin layers and surfaces. The reason is that the x radiation interacts only weakly with the material; the radiation thus penetrates deeply, so there is an averaging of the useful signal from a layer of surface atoms of interest.

It becomes possible to solve this problem thanks to the use of the x-ray optics effect known as total external reflection (Ref. 2, for example). Total external reflection has attracted interest because of, on the one hand, the appearance of an exponentially damped (evanescent) wave below the surface,[3-5] which penetrates only a very short distance into the test sample (which is an optically less dense medium), and the formation of a standing x-ray wave in the optically denser medium above the surface, on the other. This standing wave results from an interference of the incident radiation and the specularly reflected radiation.[6,7]

In the present study we have demonstrated for the first time that there is a standing x-ray wave in the region of total external reflection from a Langmuir-Blodgett (LB) film. For this purpose we detected the fluorescence from a bilayer deposited on the surface of the film and an evanescent wave which penetrated into the film, by measuring the fluorescence of heavy atoms which were part of the organic matrix.

The techniques for synthesizing LB films have been developed well; they are capable of producing structures with a fairly high quality. This quality is demonstrated clearly by x-ray diffraction[8] and experiments[9-11] which have revealed standing x-ray waves which arise in LB films in the Bragg geometry.

The test sample in the present experiments was a heterostructure consisting of 100 monolayers of lead (Pb) stearate deposited on a silicon substrate on whose surface one bilayer of barium (Ba) behenate had been deposited. The number of diffraction planes was 50, and the distance between them 49 Å.

The experiments were carried out in a two-crystal diffraction arrangement. The monochromator crystal was silicon; we used the symmetric (111) reflection and Cr $K\alpha$ x radiation with an energy of 5.4 keV. A slit 50 μm in size was positioned after the monochromator to limit the size of the beam incident on the sample at a small angle. The intensity of an x-ray reflection was measured with a NaI scintillation counter. The characteristic fluorescence (Pb $M\alpha$ from the lead stearate matrix and Ba $L\alpha$ from the barium behenate bilayer) was detected by a Si(Li) solid state detector oriented along the normal to the surface of the sample.

The fluorescence signal in the region of total reflection was measured through a one-time slow scan. In the vicinity of the Bragg reflection, the fluorescence was measured by rocking the sample repeatedly ($\sim 4 \times 10^3$ cycles) with the help of a stepping motor controlled by a special feedback system. The total count was $\sim 6 \times 10^3$ pulses for Pb $M\alpha$ and $\sim 10^3$ pulses for Ba $L\alpha$ at each point.

Theoretical calculations were carried out on the basis of the Fresnel reflection theory for multilayer structures.[12] Figure 1 shows results calculated on the distribution of the intensity of the wave field both over depth in the LB film and above its surface. These distributions correspond to various angles of incidence of the x rays in

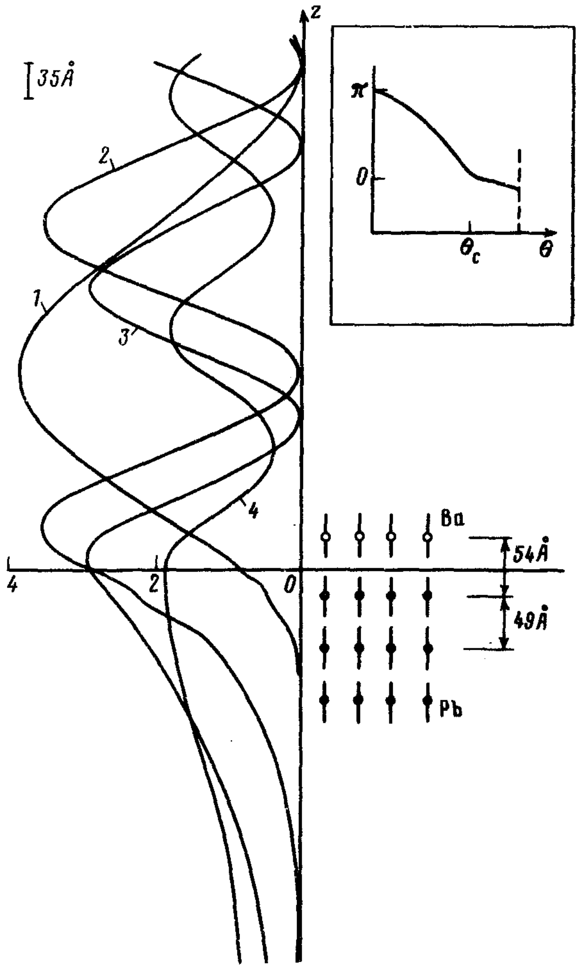

FIG. 1. Calculated distribution of the intensity of the wave field (referred to the incident surface) above and below the surface of a lead stearate sample for various values of incidence. 1—2.0 mrad; 2—3.9 mrad; 3—4.4 mrad; 4—5.0 mrad. The inset shows the angular dependence of the phase difference between the incident ray and the specularly reflected ray.

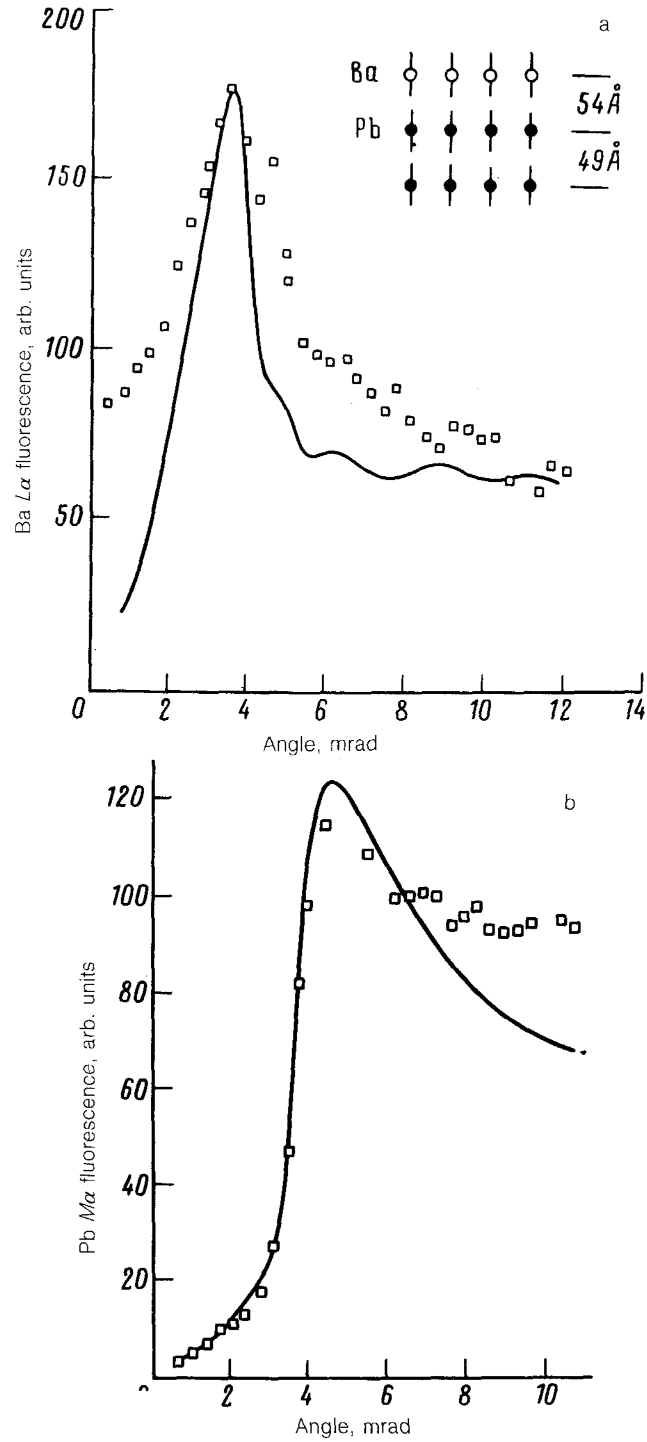

FIG. 2. Angular dependence of the fluorescence yield in the region of total external reflection for Ba $L\alpha$ and Pb $M\alpha$ (1 and 2, respectively). Points—Experimental; solid lines—theoretical.

the region of total external reflection. At angles of incidence $\theta \sim 0$, the incident and reflected rays are out of phase (see the inset in Fig. 1), forming a standing x-ray wave with an infinite period (curve 1 in Fig. 1). The first maximum (antinode) of this wave is quite far from the reflecting surface.

As the angle θ is increased from 0 to θ_c, the phase difference between the incident radiation and the specularly reflected radiation decreases to 0. This value corresponds to a shift of the first maximum of the standing wave (curve 3 in Fig. 1) toward the reflecting surface of the lead stearate film. This first maximum becomes coincident with the reflecting surface at $\theta = \theta_c$. As the angle of incidence is increased further in the region $\theta > \theta_c$, the position of the first antinode does not change; it is at the reflecting surface of the film. The amplitude of the standing wave (curve 4 in Fig. 1) decreases because of a sharp decrease in the intensity of the specularly reflected radiation.

An important feature of the standing x-ray wave in the region of total reflection is that its period D is a strong function of the angle of incidence: $D = \lambda / (2 \sin \theta)$, where λ is the wavelength of the incident radiation. The period D can reach hundreds of angstroms; this circumstance makes it possible to use a long-period standing wave of this sort to study the structure of atomic layers far above the reflecting surface.

Figures 2, a and b, shows experimental results (the points) found for a heterostructure, specifically, a bilayer of barium behenate on a Langmuir-Blodgett stearate film, along with corresponding theoretical curves (the solid lines).

To see the reason for the behavior of the fluorescence from the atoms of the barium behenate bilayer (Fig. 2a), we go back to Fig. 1. As we have already mentioned, when the test sample is scanned over the angular region $\theta < \theta_c$, corresponding to total external reflection, the antinodes of the standing x-ray wave which forms move along the direction normal to the surface. At a certain angle of incidence, the first antinode of the standing wave naturally crosses the plane formed by the barium atoms (Fig. 1). This event intensifies the interaction of the x radiation with the Ba atoms, increases the photoelectric absorption, and thereby causes a sharp increase in the yield of the Ba $L\alpha$ fluorescence which we measured.

A theoretical calculation has been carried out for a Ba–Pb distance equal to the sum of the lengths of the organic tails of the barium behenate and lead stearate molecules (54 Å). A comparison of Figs. 1 and 2 shows that the angle of incidence at which the first antinode of the standing wave coincides with the Ba plane corresponds to a maximum on the angular dependence of the Ba $L\alpha$ fluorescence yield.

To explain the behavior of the intensity of the Pb $M\alpha$ fluorescence of the lead atoms in the LB film-matrix itself, we need to take into account the angular distribution of the wave field over depth in the film under conditions of total external reflection of the incident x radiation (Fig. 1).

At small angles of incidence (near zero), the x radiation incident on the surface does not penetrate below it. It is simply "repelled" from the sample. The intensity of the wave field is naturally close to zero at any depth in this case. As a result, there is an essentially zero fluorescence yield from Pb (Fig. 2b). As the angle of incidence is increased, the evanescent wave begins to penetrate into the sample, and the intensity of the wave field in the surface layer increases as a result of the coherent interaction of the refracted and reflected waves, of roughly equal intensity, reaching a maximum at $\theta = \theta_c$ (curves 1 and 2 in Fig. 1). With increasing depth in the sample, the maximum field intensity at $\theta = \theta_c$ becomes less prominent, since the field intensity at θ_c falls off sharply because of the exponential decay of the evanescent wave. Since the resultant yield of Pb $M\alpha$ fluorescence is determined completely by the distribution of the wave field in the sample, which is a superposition of the fields in each plane containing lead atoms, the angular dependence of the Pb $M\alpha$ fluorescence yield has a maximum near θ_c (Fig. 2b).

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