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Structures of head-group and tail-group monolayers in a Langmuir-Blodgett film

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We have studied monolayer and multilayer Langmuir-Blodgett films of lead stearate using x-ray diffraction and reflectivity. We show that it is possible to distinguish the scattering due to the head groups from that due to the alkane chains. The second and subsequent alkane monolayers are distorted hexagonal (the first monolayer is known to be hexagonal); successive monolayers are shifted laterally by one-fourth of an in-plane lattice spacing, and the chains tilt by ~8° towards a nearest neighbor. The lead ion monolayers are also distorted hexagonal; successive monolayers are shifted laterally by a half lattice spacing. From rod scan intensities, we have determined the relative positions of the lead and alkane chain lattices.

Langmuir-Blodgett (LB) films receive a considerable amount of scientific attention because the technique may ultimately lead to new materials with tailored properties. These properties would result from the artificial arrangement of "head" groups, "tail" groups, or both, and thus structural information is of obvious value. However, while there have been several diffraction studies of LB films,[1–5,7] these experiments did not provide information about the different parts of the molecule. Moreover, for saturated fatty acids and salts it is known that a monolayer deposited on a glass or SiO_2 surface has a hexagonal structure,[5–7] while multilayers are predominantly distorted hexagonal,[1–6] but it is not known how the strain relaxes as a function of layer number, or even whether the first layer retains its hexagonal structure when further layers are deposited.

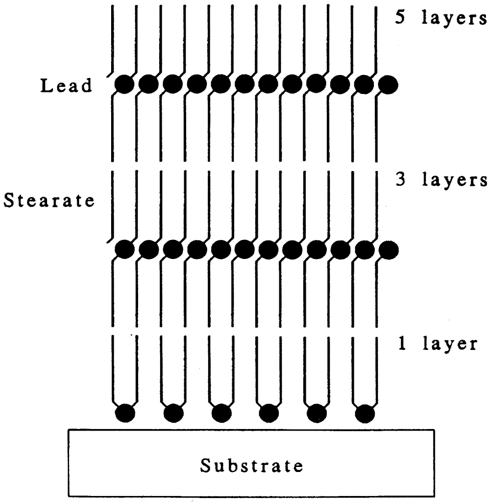

FIG. 1. Simplified view of a lead stearate Langmuir-Blodgett film.

We have used x-ray scattering to study LB films of lead stearate with 1, 3, and 5 layers (films with even numbers of layers are stable only under water). We find that the structure of the first layer is different even after subsequent layers are deposited; because of this, we are able to distinguish the scattering due to lead ions from that due to alkane chains. This in turn allows us to determine lateral positions of the lead ions relative to the alkane chains.

LB films were deposited using conventional techniques.[8–10] A 1-mM stearic acid solution was prepared in chloroform and spread on a pure water subphase containing $8.5\times10^{-5}M$ of lead acetate.[10] The *p*H of the subphase was between 5.0 and 6.5. The surface pressure was maintained at 35 dyn/cm during the deposition. Highly polished silicon wafers (purchased from Semiconductor Processing Company, Boston, MA) or window glass ($3\times1\times0.1$ in.^{3}) were used as substrates. The substrates were cleaned with a solution of Nochromix in sulfuric acid and finally plasma cleaned for 30 min before deposition. With lead stearate, as with many LB films, the first layer is deposited on an upstroke; further up-

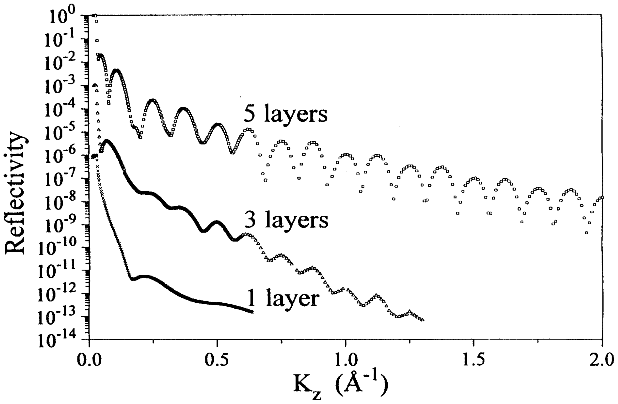

FIG. 2. X-ray reflectivity (00*l* scan) for 1-, 3-, and 5-layer LB films. The 1- and 3-layer data have been shifted down by 10^6 and 10^3, respectively, for clarity.

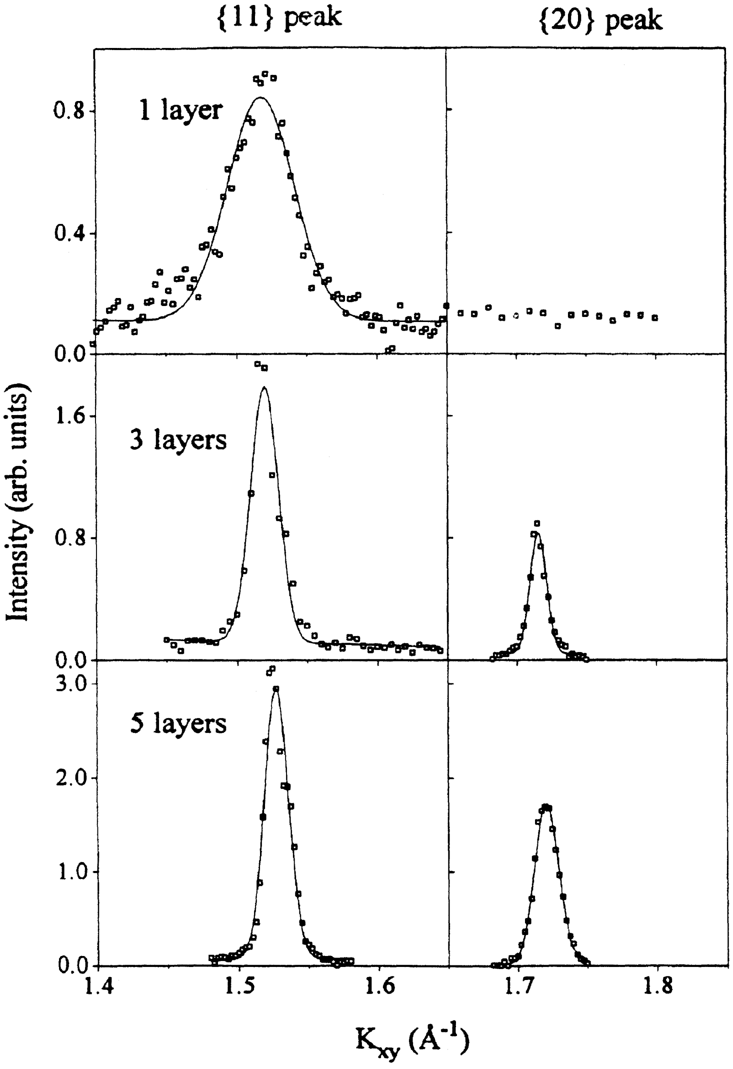

FIG. 3. Radial scans for 1-, 3-, and 5-layer LB films. The {11} peak scans for the 3- and 5-layer samples were performed at $K_z=0.19$ Å^{-1}. All other scans were performed at $K_z=0.05$ Å^{-1}. The solid lines are Gaussian fits to the data.

down dipping cycles result in two back-to-back monolayers being transferred each time ("Y-type deposition"). The schematic diagram in Fig. 1 shows the resulting layout. 1-, 3-, and 5-layer films have 1, 2, and 3 lead ion layers, respectively. Lead is divalent, but each lead monolayer (other than the first) is associated with two stearate layers; thus in Fig. 1 the lead layers and alkane chains layers have the same number density. The first lead monolayer has half the number of ions.

The x-ray experiments were performed at Beam Line X-6B of the National Synchrotron Light Source.[11] Monochromatic x rays of wavelength 1.55 Å were used, and the experiments were performed on a four-circle diffractometer. The reflectivity scans were performed in the two-circle mode of the diffractometer (fixed phi and chi, incident angle is equal to exit angle). The diffraction scans were performed in the fixed incident angle geometry.[12,13] The incident angle was 0.2°, which is slightly below the critical angle for total external reflection at this wavelength for glass and silicon. The samples were kept in a helium atmosphere during the experiment to reduce radiation damage. The monolayers are powders within the plane, and thus the diffraction vector has only two distinguishable components: in-plane (K_{xy}) and normal (K_z).

Figure 2 shows reflectivity data (scans in the K_z direction for $K_{xy}=0$) for the three LB film thicknesses. Scattering in this direction depends on the layer thickness and is not affected by whether or not the layers are ordered within the plane. We calculate the repeat distance between lead layers to be 50.3±0.2 Å from the 3-layer data and 50.6±0.2 Å for the 5-layer data. From the monolayer data we estimate a film thickness of ~20 Å.

Figure 3 shows radial scans for the three LB film thicknesses. A monolayer LB film of lead stearate shows only one diffraction peak; this means that, as previously reported for similar systems,[5-7] the monolayer has a hexagonal structure. The nearest-neighbor distance is 4.75 Å (19.54 Å^2/molecule). We did not see "superlattice" peaks corresponding to a lead monolayer with half the areal number density (~40 Å^2/molecule), and we therefore conclude that the lead ions in the first layer are disordered. The 3- and 5-layer data show two first-order radial peaks ($K_{xy}=1.525$ Å^{-1} and $K_{xy}=1.715$ Å^{-1}), which are the {11} and {20} peaks of a

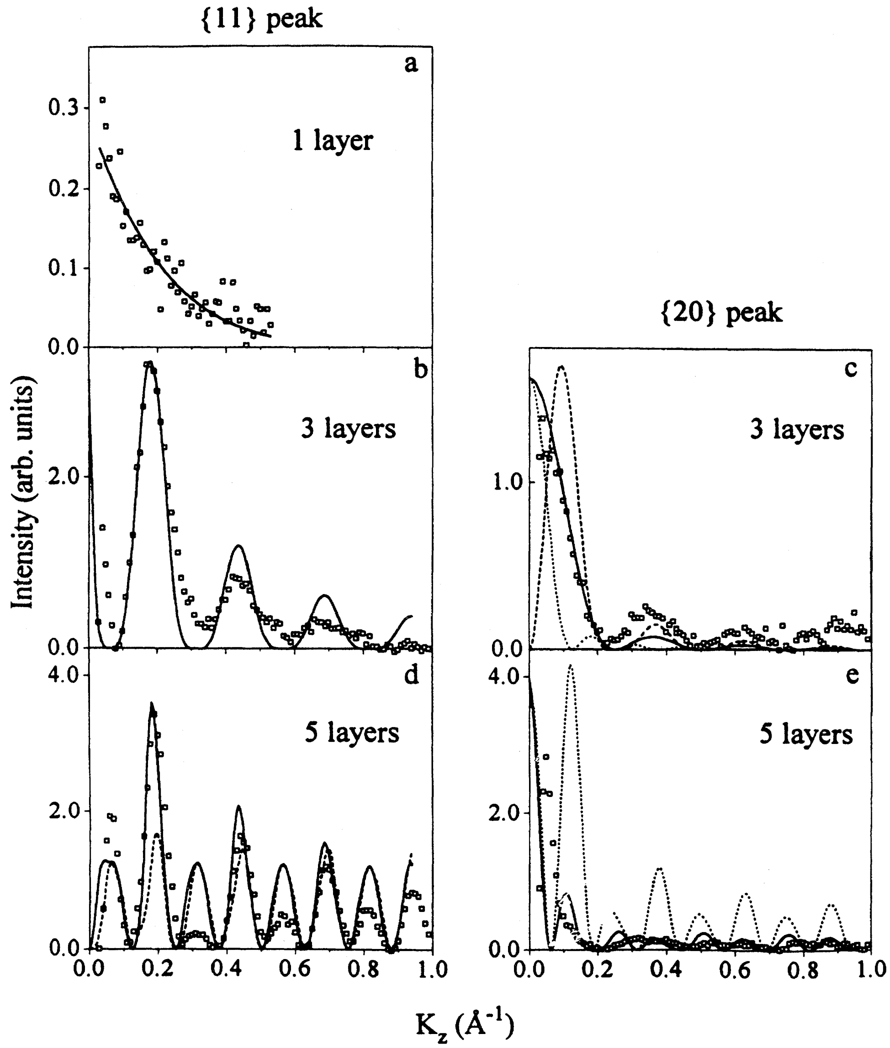

FIG. 4. "Rod" (K_z) scans at the peak positions for 1-, 3-, and 5-layer LB films. The scans at left were preformed at $K_{xy}=1.525$ Å^{-1} ({11} peak) while the scans at right were performed at $K_{xy}=1.71$ Å^{-1} ({20} peak). There is only one scan for the monolayer sample (a) as it shows only one radial peak. The solid lines are the calculated structure factors for the structure proposed in this paper. The calculations for structures shown in Figs. 5(a) and 5(b) are shown as dotted and dashed lines in (c); the solid line is the average of these two structure factors. The dashed and dotted lines in (d) and (e) are calculations for structures obtained by moving the lead ions to other symmetry positions relative to the alkane chains (see text).

distorted hexagonal structure (centered rectangular unit cell, $a=7.38$ Å, $b=4.96$ Å, 18.30 Å^2/molecule). We do not see more than one set of peaks; thus the alkane chains and the lead ions in layers beyond the first must have the same in-plane structure. The in-plane correlation lengths are ~125, 250, and 400 Å for the 1-, 3-, and 5-layer samples, i.e., the film becomes better ordered as more layers are deposited.

The intensity variations in the z direction at the diffraction peaks (rod scans) are shown in Fig. 4. The coherence lengths in the K_z direction are ~24, 50, and 100 Å for 1-, 3-, and 5-layer samples, respectively. These numbers correspond to 1-, 2-, and 4-layer thicknesses, indicating that the structure of the first layer remains distinct from the others even after the succeeding layers are deposited. The rod scan for the monolayer [Fig. 4(a)] is featureless (as expected) and the maximum intensity is at $K_z \approx 0$, meaning that the molecules are perpendicular to the substrate. The 5-layer sample shows peaks similar to those seen in earlier studies of multilayers (>50 layers) of lead stearate,[2] but *alternate peaks are missing* in the 3-layer data.

The 3- and 5-layer rod scans can be interpreted using the same structure for the 3-layer sample and the first three layers of the 5-layer sample, if we assume a unit cell with a c-axis spacing of 100 Å (not 50 Å as reported earlier[4]). Since the 3-layer sample has only one lead layer with the distorted-hexagonal structure, the intensity variations along the rod in the 3-layer data must be only due to the organic portion. Assuming that the top two layers of the 3-layer sample form half a unit cell, the peaks in Fig. 4(b) may be indexed by {113}, {117}, . . . , implying that each organic layer is displaced laterally from the previous one by $\frac{1}{4}$ lattice spacing. The {111}, {115}, {119}, . . . peaks appear in the 5-layer sample [Fig. 4(d)] but with lower intensities. We propose that these additional peaks are due to the two distorted hexagonal layers of lead ions. Our model implies that each lead monolayer is displaced by half a lattice spacing from the previous one.

To determine the direction of the shift of the organic layers we compared the major features in our experimental data to those predicted by a simple form-factor calculation: $I(\mathbf{K})=|\Sigma f_j \exp(i\mathbf{K}\cdot\mathbf{r}_j)|^2$, where the sum is over all the atoms in a unit cell. Atomic form factors were taken from Ref. 14. While the {11l} data [Fig. 4(b)] can be explained with a $\frac{1}{4}$ lattice spacing shift along either a or b (a tilt of ~8° along

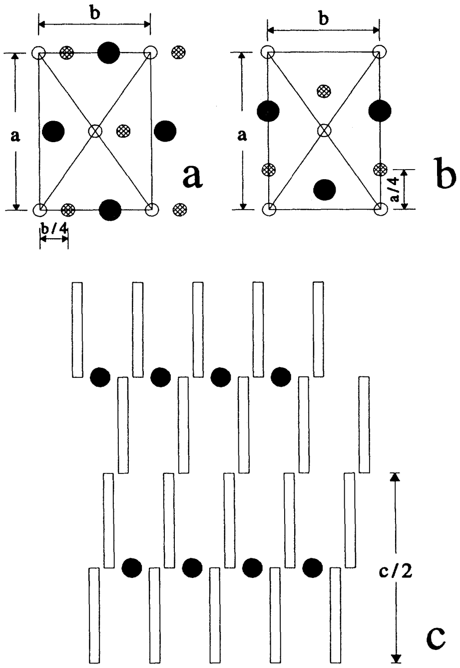

FIG. 5. Schematic diagram showing the relative positions of the lead ions and the alkane chains in a lead stearate LB film. Only two organic layers and the lead layer between them are shown in (a) and (b) for clarity. (a) Top view of a domain with layers shifted by $b/4$. (b) Top view of a domain with layers shifted by $a/4$. The large (filled) circles indicate the lead ions, while the small circles indicate the two organic layers. The second layer has been hatched to distinguish it from the first. (c) Side view of a lead stearate LB film (the first layer is not shown). The lead ions are indicated by filled circles while the alkane chain cross sections are indicated by rectangles.

the b direction was needed to match the peak positions), these do not explain the $\{20l\}$ data [the dotted and dashed lines in Fig. 4(c) show the calculations for the two shift directions; schematics of these structures are shown in Figs. 5(a) and 5(b)]. We found that the average of these two structures best matched the peaks in the data [solid line in Fig. 4(c)], suggesting that the film consists of two kinds of domains with interlayer shifts of $a/4$ and $b/4$.

It remains to determine the relative positions of the lead and alkane chain lattices. For the structure factor calculation for the 5-layer structure, we retained the structure previously determined for the alkane layers, and added the lead bilayer. We assumed that each lead ion must be laterally equidistant from two alkane chains (one from the layer above it and one from the layer below it). This allows three distinct possibilities; one is the structure shown in Fig. 5 and the other two are obtained by moving the lead ions laterally by $(0,b/2)$ or by $(a/4,b/4)$ from the positions in Fig. 5(a) and by $(a/2,0)$ or $(a/4,b/4)$ from the positions on Fig. 5(b). The dotted and dashed lines in Figs. 4(d) and 4(e) (normalization constant is arbitrary) show calculated intensities based on the latter two possibilities. The structure in Fig. 5 best reproduces the observed peak positions [solid lines in Figs. 4(d) and 4(e)], although the fit in Fig. 4(e) is not perfect. A side view of this model is shown in Fig. 5(c). The first layer, which has a different structure, is not shown in Fig. 5(c).

The structure of the alkane monolayers is the same as that proposed earlier for cadmium arachidate by Tippmann-Krayer, Kenn, and Möhwald[5] who studied 1-, 3-, and 21-layer films. However, they did not see the structure of the cation layers (their 3- and 21-layer data were qualitatively identical). Our model is different from the one proposed by Barberka *et al.*[4] for these films. They did not study a 3-layer film, which would have allowed the structure of the alkane layers to be determined separately from the cations. For the multilayers, we were able to get a better fit to the data using fewer parameters.

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