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The structure of ultrathin Langmuir-Blodgett films of cadmium behenate

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Grazing incidence x-ray-diffraction investigations of the structures of Langmuir-Blodgett films of cadmium behenate with 1, 2, 3, 5, and 21 monolayers are reported. The single monolayer film, deposited on a hydrophilic substrate, showed a hexagonal structure, whereas the bilayer film, deposited on a hydrophobic substrate, had a rectangular structure with herringbone orientation of the acyl chains. With multilayer films formed on a hydrophilic substrate, it was possible to detect that the hexagonal structure of the first layer was retained when additional layers were deposited and that the additional layers had the same rectangular structure as the bilayer. © 2005 American Institute of Physics. [DOI: 10.1063/1.2131067]

I. INTRODUCTION

In an earlier work,¹ multilayer Langmuir-Blodgett (LB) films of cadmium arachidate (CdAr) were shown by grazing incidence x-ray diffraction (GIXD) to have a structure in which the Cd atoms are arranged in a monoclinic (*C*) structure and the hydrocarbon chains have a monoclinic (*P*) structure with their long axes normal to the film surface and arranged in a herringbone pattern. Both structures have the same parameters of the unit cell: $a=7.52 \text{ \AA}$, $b=4.86 \text{ \AA}$, $c=55.4 \text{ \AA}$, $\alpha=\gamma=90^\circ$, and $\beta=87.5^\circ$, giving an area per molecular chain of 18.3 \AA^2 in the film plane. In addition, there is a one-dimensional superstructure in the film plane with a spacing of 18.8 \AA ($d_{2/5 \ 0}$) along the $[10]$ direction, corresponding to a 5×1 commensurate superstructure. It was also pointed out that multilayer films of both cadmium behenate (CdBe) and cadmium stearate (CdSt) have structures with the same symmetry as CdAr.

There has been other work over the past two decades in which the structures of LB films of soaps of long-chain fatty acids have been carefully studied with grazing incidence x-ray and electron diffractions.² Generally, these studies have demonstrated that multilayer films of the cadmium soaps have a rectangular in-plane structure with the molecular chains normal to the film surface regardless of the number of layers, whereas the single monolayer LB films exhibit hexagonal packing with long-range bond orientational order and a short-range positional order.

More recently, Dupres *et al.*,³ also with GIXD, have

probed the structures of Langmuir and LB films of CdBe. Their results from the Langmuir films are very similar to those from the Langmuir films of some long-chain fatty acids (spread on pure water) published previously.⁴ However, for the LB films of one, three, and five layers their results are quite different from those reported in the literature.² Dupres *et al.* found that the single monolayer film had a rectangular structure with chains normal to the surface and that the three- and five-layer films had similar structures but with the molecular chains tilted by 1° – 6° .

Our present contribution to this question is a set of GIXD results from the LB films of 1, 2, 3, 5, and 21 monolayers of CdBe. These data differ significantly from those of Dupres *et al.* The single monolayer film has a hexagonal structure with an apparent thickness slightly less than that expected for fully extended chains normal to the substrate surface. This feature together with a molecular area slightly larger than that required for close-packed chains indicates a rotator phase with some gauche bonds in the chains. Bilayers in the multilayer films have a rectangular in-plane structure with the acyl chains fully extended and perpendicular to the film surfaces and a herringbone orientation of the chains. In multilayer films with an odd number of layers, the first layer (with the polar group in contact with the substrate) has now been shown to exhibit the same hexagonal structure as that observed in the monolayer film.

II. EXPERIMENT

The LB films of CdBe were prepared by the vertical deposition mode.⁵ Behenic acid (>99.5%, Hormel Foundation) was dissolved in chloroform (Spectroscopic Grade, Merck) at a concentration of 2.0×10^{15} molecule μL^{-1} for use as the spreading solution. The subphase was prepared

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with CdCl_2 (AR Grade, Sigma) dissolved in Milli-Q water to a concentration of $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ and adjusted to pH 7.0 using KHCO_3 ($7.5 \times 10^{-5} \text{ mol dm}^{-3}$). Polished silicon wafers [(111) surface, Semiconductor Processing Company, Boston, MA] were used as substrates after cleaning by RCA standard procedure B.⁶ LB deposition was performed at a surface pressure of $29 \pm 1 \text{ mN m}^{-1}$ and a dipping rate of 0.1 mm s^{-1} at room temperature. The two-layer films were formed on substrates with hydrophobic surfaces, prepared in the way previously reported.⁷ In all cases the transfer ratio was unity on both up and down strokes. The films were stored in a sealed case and measured with GIXD within 6 days of preparation.

The x-ray-diffraction experiments were carried out at the Australian National Beamline Facility (ANBF) located at Beamline 20B of the Photon Factory in Tsukuba, Japan. The experimental setup, the convention regarding coordinate frame choice, and the data reduction have been described elsewhere.^{8,9} The measurements were performed in a moderate vacuum (<0.1 Torr). A monochromatic and horizontal x-ray beam with a wavelength of 1.739 \AA and a dimension of $1.0 \times 0.05 \text{ mm}^2$ was incident on the sample at an angle of 0.18° (ca. 0.75 of the critical angle for total external reflection on SiO_2/Si but greater than that on CdBe). Imaging plates used to collect the diffraction signals were mounted in a camera at a distance of 400 mm from the sample.⁹ Because there is no collimating element before the detector in this system, the resolution of the experiment is determined by the footprint of the beam on the sample, which is limited by the width of the film (1.0 cm), effectively acting as a slit. With this arrangement the resolution in Q_{xy} is dependent on the scattering angle and is approximately 8 mrad (0.03 \AA^{-1}) at $Q_{xy} = 1.5 \text{ \AA}^{-1}$. The exposure time was 120 s. All measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

It is clear from Fig. 1 that the diffraction pattern from the single monolayer film differs markedly from those of the multilayer films, indicating significant differences between the in-plane structures. Consequently, one of the major questions to be asked of these results is whether the different structure of the first layer persists when subsequent layers are deposited on top of it, or whether the first layer changes to better accommodate the superimposed layers. To facilitate discussion of this point, the diffraction pattern from the single monolayer film will be discussed first, followed by general discussion on the information gained from the diffraction patterns of the multilayer films, and finally we address the specific differences related to the bilayer film and the unique structure of the first layer.

A. Single monolayer film

Figure 1 shows the diffraction pattern from a single monolayer film of CdBe , including the diffraction in both the high Q_{xy} range and the diffuse scattering. (That is, a vertical profile taken along Q_z from the point where $Q_{xy} = 0$. We have previously called this information the “meridional diffraction,” but for consistency with other authors it will be re-

ferred to as the “diffuse scattering” in this paper.) In the high Q_{xy} range, there is a single broad in-plane diffraction spot at $Q_{xy} = 1.52 \text{ \AA}^{-1}$ (corresponding to a d spacing of 4.13 \AA). This suggests that the molecules in the film are hexagonally arranged with their long axes, on average, perpendicular to the surface of the film. The area per chain in the film plane is 19.7 \AA^2 , large enough to allow rotation of the chains,¹⁰ and the in-plane correlation length calculated from the broad peak is 42 \AA . This determination is in excellent agreement with those reported by others using GIXD, electron diffraction, and atomic force microscopy (AFM) techniques^{8,10-13} but differs from that of Dupres *et al.*³

It should be pointed out, however, that the conditions for deposition used by Dupres *et al.* differ from those used in the present work and by others:^{1,11,14} a slightly lower pH , a much lower Cd^{2+} concentration ($1.9 \times 10^{-6} \text{ mol dm}^{-3}$ compared with $2 \times 10^{-4} \text{ mol dm}^{-3}$ or higher), and a significantly higher surface pressure (35 mN m^{-1} compared with 29 mN m^{-1}). These differences could explain why the results of Dupres *et al.* differ from those in the current and other published works.

The diffuse scattering as measured in this experiment is sometimes described as off-specular scattering, although the latter term is used in different ways in the literature.¹⁵ In principle this scattering contains information about the structure normal to the interface and also the out-of-plane fluctuations.¹⁶ To our knowledge this is the first time that the diffuse scattering from a single monolayer LB film has been reported. In practice fitting of the scattering collected from imaging plates is complicated by the difficulty of absolute normalization and removal of background. As a first approximation the data from the monolayer were fitted to a simple box model, from which we determined that the thickness of the film is $26.3 \pm 0.3 \text{ \AA}$, less than the length of a fully extended molecule (about 30 \AA). Because of the scaling problem, electron densities obtained from this model are considered unreliable, but the thickness which is mainly determined from the positions in Q_z of the minima is nevertheless accurate. With x-ray reflectivity measurements of a single monolayer of lead stearate (PbSt) on a silicon wafer, Malik *et al.*¹² also observed that the thickness of the film is 5 \AA less than the fully extended chain of the soap. There are two possible explanations for the lesser thickness: gauche defects in the molecular chains and tilting of the molecular chains. To account for the measured thickness, the angle of tilt of fully extended behenate chains from the surface normal would be 29° . This is slightly higher than the tilt angles reported by Garoff *et al.* (25° in a cadmium stearate monolayer deposited at 10 mN m^{-1} , measured by electron diffraction)¹³ and Ahn and Franses (23° - 26° in a monolayer of lead stearate).¹⁷ However, a tilt angle of 29° requires a shift of 14 \AA at the top end of the behenate chain so it is difficult to see how a shift of this magnitude could be accommodated while maintaining the average tilt of 0° required by the position of the diffraction spot at $Q_z = 0$. The area per molecule is larger than that required for close-packed perpendicular chains, indicating a rotator phase, so it is likely that there are some gauche bonds present in the structure, leading to a thinner film. Hence the tilting of fully extended chains seems a less likely structure

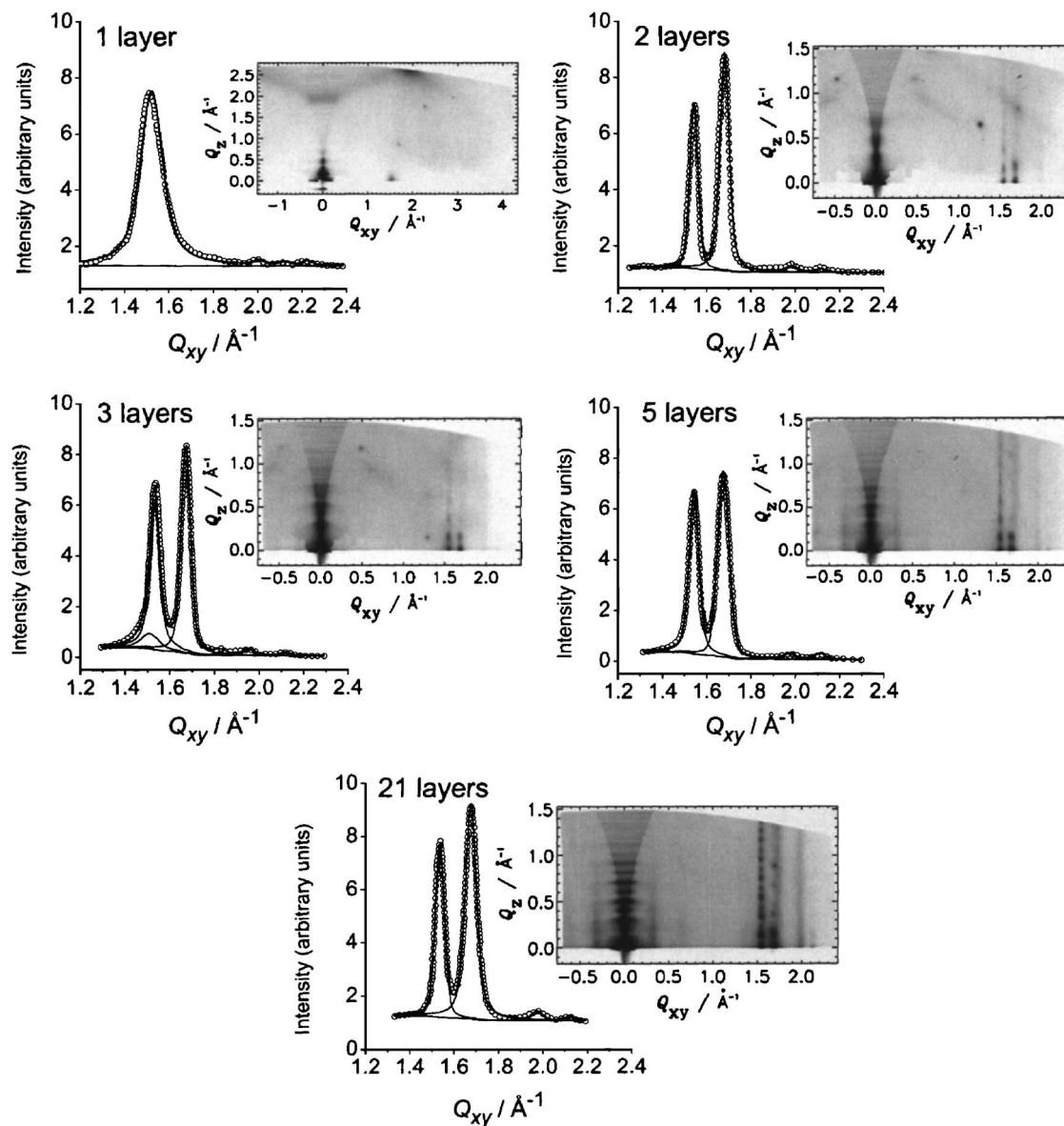


FIG. 1. Image plate diffraction patterns and in-plane profiles of the GIXD patterns (at $Q_z \approx 0$) from the 1, 2, 3, 5, and 21 monolayers LB films of CdBe. The intensities have been scaled by the following factors: 1 layer, $\times 16$; 2-layer, $\times 8$; 3-layer, $\times 4$; 5-layer, $\times 3.3$; and 21-layer, $\times 1$.

than rotating chains with some gauche bonds. It should also be noted that the diffuse scattering arises from the average film structure in the out-of-plane direction, which may include amorphous domains that would not contribute to the in-plane diffraction.

B. Multilayer films

The diffraction patterns from the multilayer films (2, 3, 5, and 21 layers) of CdBe are also shown in Fig. 1. The general pattern corresponds closely to the pattern reported previously for a 27-layer film of CdAr,¹ and the interpretation will therefore be almost identical. The main features are the two strong sets of diffraction spots at Q_{xy} values of 1.54 and 1.68 \AA^{-1} corresponding to d spacings of 4.08 and 3.74 \AA . These spots can be indexed as (11 l) and (20 l), respectively, and attributed to a rectangular in-plane structure with lattice constants of $a=7.52$ \AA , $b=4.86$ \AA , and $\gamma=90^\circ$. The

other diffraction sets can then be indexed as for CdAr. Of particular interest are the two weak spots located at Q_{xy} of 2.12 \AA^{-1} ($d_{xy}=2.96$ \AA^{-1}) and most clearly visible in the thicker films. This set can be indexed as (21) ($h+k=\text{odd}$), indicating that the acyl chains in the film are packed in a herringbone mode as discussed elsewhere.^{1,7} Because of this herringbone arrangement of the acyl chains there are 2 molecules/unit cell and hence a molecular area of 18.3 \AA^2 molecule⁻¹.

Although the relative intensities of the (11) and (20) peaks agree approximately with those reported previously for CdAr,¹ a very different pattern was found by Tippmann-Krayer *et al.*¹¹ They observed that the intensity of the (11) peak was significantly greater than that of the (20) peak. This can be attributed to the different detection methods employed in the two measurements. The plots in Fig. 1 arise from a scan of the in-plane diffraction intensities on the imaging plate, whereas the scans of Tippmann-Krayer *et al.* are the

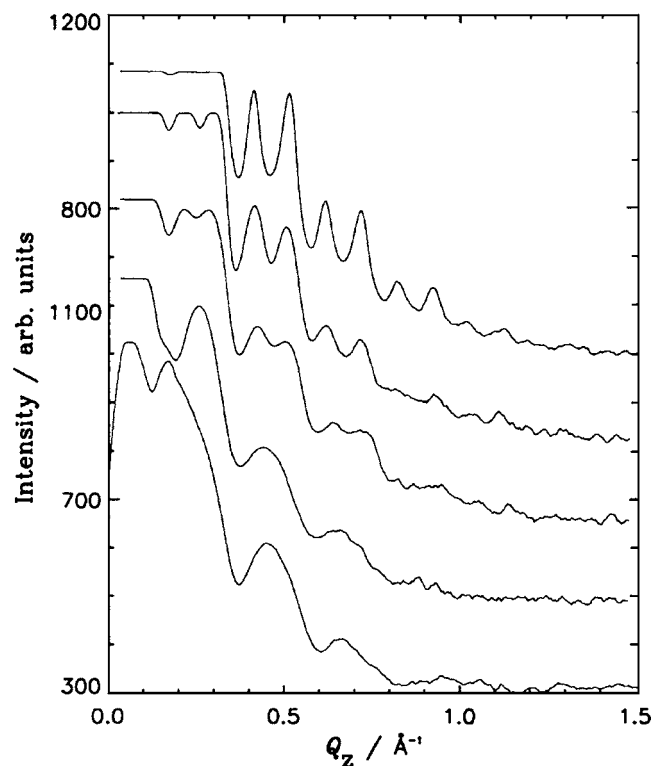


FIG. 2. Profiles of the diffuse scattering diffraction (logarithmic intensity scale). The profiles from the bottom to the top are from the 1-, 2-, 3-, 5-, and 21-layer films.

integrated intensities from a Soller collimator and a position-sensitive detector and thus include the out-of-plane spots.

Mention should also be made of some other diffraction features (Fig. 1), particularly noticeable in the thicker films: firstly, a pair of rods at Q_{xy} of $\pm 0.334 \text{ \AA}^{-1}$ symmetrically located about the direct beam position and, secondly, two rods at Q_{xy} of 1.75 and 1.99 \AA^{-1} . Such rods arise from a superstructure in the film¹ and have also been observed with multilayer films of CdSt and CdAr.

As discussed previously,¹ the diffraction intensities along Q_z arise from the superposition of spots from the cadmium atoms, decreasing only slowly with Q_z , and spots from the acyl chains, decreasing rapidly with Q_z . Thus the diffraction from the cadmium atom layers is clearly observable in the Q_{11l} set of the 21-layer film (at 1.54 \AA^{-1}) up to $l=13$, the limit of the measurement.¹ The Q_{001} value calculated from the peaks of the $(11l)$ set (see Fig. 2) is 0.105 \AA^{-1} . Thus $d_{001}=59.8 \text{ \AA}$, equal to a bilayer thickness of CdBe with fully extended acyl chains perpendicular to the surface of the film.

The diffuse scattering from the 21-layer film of CdBe is similar to that from the 27-layer film of CdAr, but with different scaling along Q_z . The spacing between major minima is 0.21 \AA^{-1} giving a d spacing of 29.9 \AA .

The structure of the two-layer LB film is significant because a bilayer is the basic unit of a multilayer LB film and is considered to determine the structure of multilayer films, particularly their in-plane structure. Furthermore, the x-ray diffraction from the odd-numbered layer films can be considered as the addition of the first monolayer and the following bilayers. It is therefore important to note that the in-plane diffraction pattern from the two-layer film (Fig. 1) is identi-

cal to that from the 21-layer film where the influence of any different first layer would be negligible. Up to now no determination by x-ray diffraction of a two-layer LB film of soaps has been reported.

It is reasonable to assume that where the interaction between a layer and its adjacent layer, or between a layer and the substrate, is determined by cadmium-mediated carboxylic acid head group interactions it will be stronger and more likely to influence the structure than a chain-chain interaction. In contrast to the other multilayer films, the two-layer film was built with the terminal methyl groups of the molecules in the first monolayer contacting the hydrophobic substrate. Therefore the interaction of this first layer with the substrate is probably weaker than that found in the odd-numbered layer films, and it is likely that the first layer's structure will be influenced by the deposition of a strongly interacting second layer when the substrate is withdrawn from the subphase. This is in contrast to the other multilayer films, where head groups are in contact with the substrate and have different chemical compositions from the head groups in (head-to-head) bilayers, making a structural difference likely.¹³ Furthermore, the interaction with a superimposed layer is chain to chain and so relatively weak. This point will be investigated in more detail in the next section.

Figure 1 shows that there are high-order diffraction spots along Q_z in the (11) and (20) sets of the two-layer film, implying that the film has a three-dimensional or lamellar structure. Since in the two-layer film there is only one layer of cadmium atoms, the high-order diffraction must come from the two layers of acyl chains. The spacing in Q_z between two neighboring spots (Q_{00l}) in the (11) set (but not between the first and the second spot) is 0.214 \AA^{-1} (Fig. 3), corresponding to a d spacing (d_{001}) of 29.5 \AA which is equal to the length of a CdBe molecule with a fully extended acyl chain. This spacing is equivalent to that calculated from the diffuse scattering from the two-layer film (Fig. 2). The value of d_{001} together with the in-plane locations of the first spots in the (11) and (20) sets indicates that the molecular chains are normal to the surface of the film. These values are in good agreement with those from the 21-layer film.

It is interesting that in all of the multilayer films the second spots in the (11) and (20) sets are located at Q_z of 0.14 ± 0.01 and $0.17 \pm 0.01 \text{ \AA}^{-1}$, respectively. Their location is possibly due to the relative positions of the chains in the two different layers. In other words, the axes of the two chains attached to a single cadmium atom may not be aligned but may be offset in opposite directions from the cadmium atom while the individual chains are normal to the film surface. Consequently, the third, c , axis of the unit cell must be tilted from the normal to the film surface. That determines the observed out-of-plane behavior of the second spots in both the (11) and (20) sets. As such, the calculated¹⁸ tilt angle and the azimuthal angle of the tilting from [10] direction are 4.8° and 34° , respectively.

C. Structure of the first layer

A multilayer film with an odd number of layers is composed of a single monolayer film, followed by a certain num-

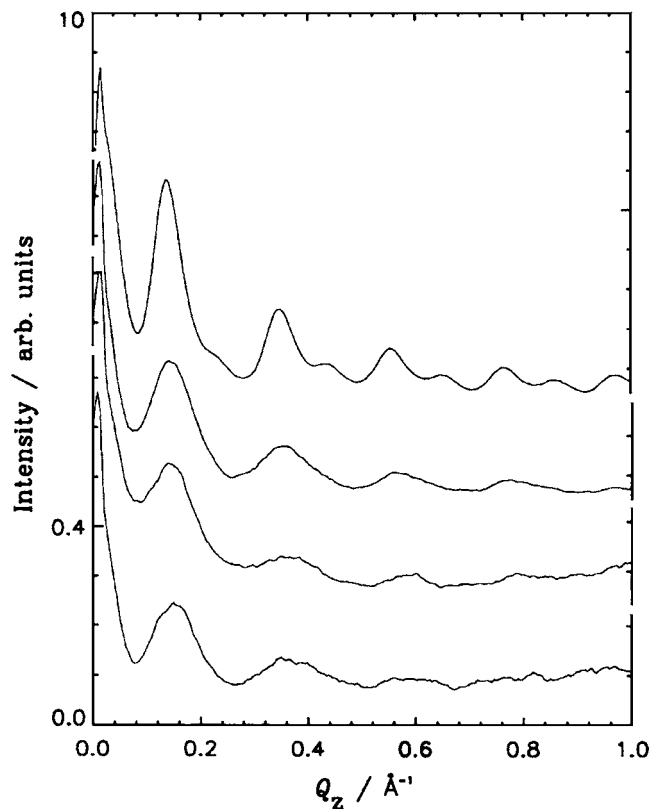


FIG. 3. Profiles of (11l) diffraction sets. The profiles from the bottom to the top are from the 1-, 2-, 3-, 5-, and 21-layer films.

ber of bilayers deposited above it. By examination of the x-ray-diffraction pattern in Fig. 1, it should be possible to answer the important question of whether, in multilayer film formation, the first layer retains its hexagonal structure or rearranges to accommodate the rectangular structure of the following bilayers. If the structure of the first layer is retained, the x-ray-diffraction pattern should comprise a superposition of the hexagonal monolayer and the rectangular bilayer structures. Clearly the relative contribution of the hexagonal structure would be greatest in the three-layer film and would decrease as the number of layers increases. Our results show (Fig. 1) that there is a general similarity in the diffraction pattern of the 3-layer film to those obtained from the 2-, 5-, and 21-layer films. There is, however, a somewhat broader base to the peak at 1.54 \AA^{-1} in the three-layer film and to a lesser extent in the five-layer film, but whether this is significant requires a more detailed analysis.

For the fatty acids of interest here, the single diffraction peak from the monolayer has a Q_{xy} value (1.52 \AA^{-1}) that is very close to that of the (11) peak from the bilayers (1.54 \AA^{-1}), so the two peaks would merge with summation of their intensities. However, the (20) peak from the bilayer(s) is clear of the diffraction from the monolayer, and this enables us to analyze the intensity of the (11) peak relative to the (20) peak in order to test for the presence of the hexagonal structure. If, on the other hand, the first layer rearranges to match the superimposed bilayer structure, only the diffraction pattern from the rectangular structure should be observed, independent of the number of layers. In this case the relative intensities of the (11) peak to the (20) peak should remain constant.

TABLE I. Areas (in arbitrary units) of the two major peaks in the profiles taken at $Q_z=0$ from each of the diffraction patterns in Fig. 1. Peak 1 refers to the (11) peak at 1.54 \AA^{-1} , while peak 2 refers to the (20) peak at 1.68 \AA^{-1} . Note that each profile was scaled differently, so comparisons between absolute areas are not significant, but the ratios may be compared.

No. of layers	Total area peak 1	Total area peak 2	Ratio peak 1/peak 2
1
2	0.308	0.495	0.62
3	0.508	0.512	0.99
5	0.417	0.524	0.80
21	0.372	0.649	0.57

The diffraction peaks have been fitted with functions derived from a mix of Lorentzian and Gaussian distributions. The percentage Gaussian was allowed to vary for each peak and, for the majority of larger peaks, was in the range of 20%–60%. In this way it has been possible to deconvolute the two major peaks of the in-plane profiles for the multilayer films and determine the areas under each peak. The ratios from the films of different layers are shown in Table I. It can be seen that the ratio for the 2-layer film agrees well with that from the 21-layer film, however, the ratios for the 3- and 5-layer films are much greater and decrease with the number of the layers. This indicates a significant contribution to the intensities of the peak at 1.54 \AA^{-1} in the odd-numbered films from another source, which must be the hexagonal structure of the first layer with a peak maximum at $Q_{xy}=1.52 \text{ \AA}^{-1}$. In fact, for the three-layer structure, the fit was significantly improved by the inclusion of a small peak centered at 1.52 \AA^{-1} , which can be seen in Fig. 1. The area for peak 1 given in Table I includes this peak.

A simple analysis can be made based on the assumption that the intensities from the multilayer films are the linear addition of those from the first monolayer and from the following bilayers deposited. We begin with the assumption that any contribution from the first monolayer to the intensities measured for the 21-layer film is negligible. If we label the intensity of peak 1 I_{11} and that of peak 2 I_{20} , then from the 21-layer film the ratio $I_{11}/I_{20}=0.57$. Taking the intensities from the other films to be linear combinations, the three-layer film intensity ratio is $(I_{11}+I_h)/I_{20}=0.99$, where I_h is the intensity contribution from the first monolayer. Hence $I_h/I_{20}=0.42$. We can therefore predict that for the five-layer film, which consists of a monolayer and two bilayers, the ratio should be $(2I_{11}+I_h)/2I_{20}=0.78$. This is in excellent agreement with the experimental value of 0.80.

Further information on the relative structures of the first and subsequent layers could in principle be obtained from the diffuse scattering, as it has been shown that this scattering can produce information of superior quality to that obtained from specular reflectivity.¹⁶ Because the molecular area of the first monolayer (19.7 \AA^2) is significantly different from that of the subsequent layers (18.3 \AA^2) it is reasonable to expect that the electron densities obtained from fitting the diffuse scattering to a box model would be slightly different for the first and subsequent layers. Unfortunately detailed fitting of our data to obtain accurate electron densities was

not possible due to the previously mentioned uncertainties in scaling and background due to the use of image plates.

Previous diffraction results from ultrathin films of CdAr (Ref. 11) and PbAr (Ref. 12) deposited under similar conditions to the present study have been published, and the basic structural features including the hexagonal monolayer and rectangular multilayer structures were also observed by both teams of researchers. However, evidence of the differing structure of the first monolayer in odd-numbered multilayer films has not previously been reported. The structures observed by Dupres *et al.*³ differ from those in the current work and in previous studies, and the likely explanation is that the very low Cd²⁺ concentration and low pH used during deposition may have given a mix of the acid and cadmium salt in the deposited LB films. It is also possible that the high surface pressure used during deposition (35 mN m⁻¹) could cause buckling during film deposition.

IV. CONCLUSIONS

Using GIXD the structures of 1-, 2-, 3-, 5-, and 21-layer LB films of CdBe were investigated, and, in particular, the structure of a 2-layer LB film was observed for the first time. Diffraction data in a large area of Q space (including diffuse scattering) were collected with the use of two-dimensional detection. The single monolayer LB film has a hexagonal structure of a short-range positional order with the molecular chains in a rotator phase with some gauche bonding.

The bilayer film has a rectangular in-plane structure with the molecular chains normal to the film surface. The chains are arranged in herringbone mode and the zigzag plane of the C–C chain at one corner of the unit cell is orientated from the [10] direction by about 34°.

Three-dimensional diffraction patterns were observed from all of the multilayer films probed. In multilayer films

the first layer, if deposited by raising the substrate through the floating monolayer, has a hexagonal structure and the subsequent layers, regardless of their number, have the same rectangular in-plane structure and herringbone molecular chain orientation as a bilayer film. The hexagonal structure in the first monolayer is retained when the following bilayer film is deposited on it.

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