J. Am. Chem. Soc. 1994, 116, 7903–7904

Extended-Lattice Langmuir–Blodgett Films: Manganese Octadecylphosphonate Langmuir–Blodgett Films Are Structural and Magnetic Analogs of Solid-State Manganese Phosphonates

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Received March 21, 1994

Layer-by-layer deposition procedures offer the promise of controlling, on a molecular level, the physical properties of organic or mixed organic/inorganic thin films. While there are now many examples[1] of assemblies designed with specific optical,[2,3] nonlinear optical,[4–6] or electronic properties[7–11] in mind, there are far fewer reports[12–14] of magnetic phenomena in Langmuir–Blodgett (LB) or organic self-assembled (SA) films. A reason may be that the high degree of in-plane crystalline order needed to observe cooperative magnetic phenomena is not always present in LB or SA films. One route to ordered LB films is to target LB analogs of layered solid-state materials. As a result of this approach, we report the preparation of crystalline inorganic extended lattice monolayers, formed using LB methods, and present evidence for short-range magnetic order in these LB films. LB layers of manganese octadecylphosphonate ($Mn(O_3PC_{18}H_{37})\cdot H_2O$) are shown by transmission electron diffraction to possess in-plane crystalline order that is analogous to the in-plane structure of the known solid-state manganese phosphonates.[15,16] Temperature dependent spin susceptibility and EPR line-width analyses provide evidence for antiferromagnetic exchange and short-range antiferromagnetic order within the LB layers.

The transition metal phosphonates[15–18] are examples of mixed organic/inorganic extended-lattice layered solids.[19] Alkylphosphonate and phenylphosphonate salts of several divalent[15,16] metals, including Mn^{2+}, have been studied by powder X-ray diffraction, and while the interlayer spacing depends on the size of the organic group, the in-plane spacing is nearly independent of the divalent metal ion or the organophosphonate ligand.[15,16] Manganese phenylphosphonate[15,16] ($Mn(O_3PC_6H_5)\cdot H_2O$), the only manganese member of the series for which single-crystal structural data are available, crystallizes in an orthorhombic space group with a = 5.73 Å, b = 14.33 Å, and c = 4.95 Å. We have previously prepared a powder sample of $Mn(O_3PC_6H_5)\cdot H_2O$ and have observed an antiferromagnetic ordering transition at 12 K by SQUID magnetometry.[20] Carling et al.[19b] have shown that the series $MnC_nH_{2n+1}PO_3\cdot H_2O$ (n = 1–4) are all canted antiferromagnets with ordering temperatures in the range 14.8–15.1 K. The manganese octadecylphosphonate films described here are fabricated in order to determine if extended-lattice LB films can be prepared and serve as structural and magnetic models for the bulk manganese organophosphonates.

Manganese octadecylphosphonate LB films are prepared by spreading octadecylphosphonic acid on an aqueous subphase that is 5×10^{-4} M in $MnCl_2\cdot 4H_2O$ and held in a pH range of 5.2–5.5. Pressure versus area isotherms yield a mean molecular area of 27 Å^2 and are slightly expanded relative to that of octadecylphosphonic acid on a metal-free subphase.[21,22] The Langmuir monolayers are compressed to a target pressure of 17 mN/m, and bilayers are deposited onto hydrophobic supports using transfer speeds of 8 mm/min on the downstroke and 5 mm/min on the upstroke. Transfer ratios are consistently in the range 0.98–1.05. We postulate that the slow deposition speed on the upstroke allows the film to drain and aids in the crystallization of the organic/inorganic lattice. XPS analyses of both single-bilayer and multilayer films show that Mn and P are present in a 1:1 ratio, which is consistent with the stoichiometry of the bulk manganese phosphonates.[15,16] Infrared spectra from 900 to 4000 cm^{-1} were obtained for films deposited onto Ge ATR crystals. The frequency and line shape of the C–H stretching bands are characteristic of crystalline hydrocarbon chains.[23–25] In addition, two sharp bands are observed at 978 and 1088 cm^{-1} that can be assigned to the symmetric and asymmetric PO_3^{2-} stretching modes, respectively,[26,27] and a band at 1608 cm^{-1} can be assigned to a H_2O bending mode. The intensity of each IR band is proportional to the number of deposited bilayers, indicating that the deposition cycles are uniform. This is confirmed by ellipsometry, which shows that the total film thickness increases linearly with the number of bilayers.[28] The layered structure of the films is demonstrated by X-ray diffraction,[29] where an interlayer spacing of 48.5 Å is determined from 4 orders of diffraction from a 10-bilayer film.

The in-plane structure of the manganese octadecylphosphonate film is seen by transmission electron diffraction (TED),[30] where the LB film gives rise to a diffraction pattern of sharp rings (Figure 1). The pattern in Figure 1 is from a 2.6 μm diameter area of

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(28) Ellipsometric measurements were performed with a Rudolph Instruments Series 431A universal ellipsometer. A film thickness per bilayer of 49 Å ± 3 Å was determined using a film refractive index of 1.6.

(29) X-ray diffraction in reflection geometry was performed with a four-circle diffractometer using an 18-kW rotating anode source producing Cu Kα radiation.

(30) TED experiments were performed on a JEOL JEM 200CX electron microscope. In all cases a 100-kV accelerating voltage was directed normal to the ac plane of the sample. During the experiment the sample was kept at liquid nitrogen temperature.

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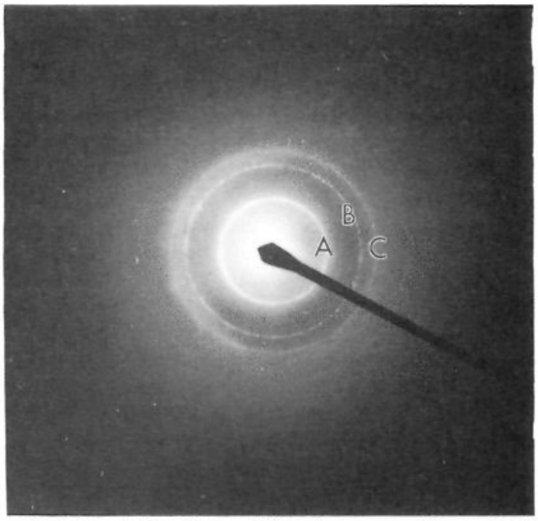

Figure 1. Transmission electron diffraction pattern from a 10-bilayer manganese octadecylphosphonate LB film. The labeled rings are assigned to the *hkl* reflections, A = {110}, B = {120}, and C = {300}, and correspond to an orthorhombic space group with unit cell parameters a = 5.7 Å and b = 4.9 Å.

a 10-bilayer film and arises from domains of crystalline order that average about 100 nm^2 in size, as determined from dark field TEM images. The domains are randomly oriented within the plane of the film (ac plane), resulting in the circularly averaged diffraction rings. This diffraction does not arise from hexagonal close-packing of the organic chains that is normally observed in LB films of metal salts of fatty acids,[31] nor can the diffraction pattern be assigned to purely inorganic manganese species that might have formed during the deposition procedure. The d-spacings can be assigned to an orthorhombic unit cell and, coupled with the interlayer spacing determined from X-ray diffraction, yield unit cell parameters a = 5.7 Å, b = 48.5 Å, and c = 4.9 Å for the LB film. The a and c lattice constants are nearly the same as those of the phenyl, methyl,[15,16] and decyl[32] manganese phosphonates (Table 1), demonstrating that the manganese octadecylphosphonate LB film is a structural analog of the bulk manganese organophosphonates.

Figure 2 shows the integrated area of the EPR signal plotted as a function of temperature from 300 to 10 K. The integrated area, which is proportional to the spin susceptibility, gradually increases with decreasing temperature to a maximum near 30 K, before decreasing at lower temperatures until the signal disappears around 18 K. The shape of the plot is characteristic of antiferromagnetic exchange in a low-dimensional lattice.[12,33-35] A numerical expression for the susceptibility of a quadratic-layer Heisenberg antiferromagnet, eq 1, has been derived by Rushbrooke and Wood:[35]

$$Ng^2\mu_B{}^2/\chi = 3\theta + \sum(C_n/\theta^{n-1}) \qquad (1)$$

where $\theta = kT/JS(S+1)$, g is the Lande factor, N is the number of spins, μ_B is the Bohr magneton, and J is the antiferromagnetic exchange constant defined from the spin Hamiltonian $H = J\sum S_iS_j$ where i and j represent nearest neighbors. Using the coefficients, C_n, derived by Lines[34] for $S = {}^5/_2$, we have fit the data for a T_{max} of 30 K yielding a value of J/k = 3 K. Also plotted in Figure 2 is the change in line width as a function of temperature, which increases slightly as the temperature is lowered toward 30 K. Near the temperature of maximum susceptibility and below, the line width increases dramatically until the signal can no longer be observed near 18 K. Such behavior is characteristic of layered antiferromagnetis[12,33,36] and results from the increased coherence length of the short-range antiferromagnetic order. Magnetic exchange in an LB film has previously been observed in only one other example,[12-14] manganese stearate, first studied by Pomerantz.

Table 1. Unit Cell Parameters for Bulk and LB Films of $Mn(O_3PR){\cdot}H_2O$

compound	a, Å	b, Å	c, Å
$Mn(O_3PC_6H_5){\cdot}H_2O^a$	5.73	14.33	4.95
$Mn(O_3PCH_3){\cdot}H_2O^a$	5.82	8.79	4.91
$Mn(O_3PC_{10}H_{21}){\cdot}H_2O^b$	5.86	30.6	4.91
$Mn(O_3PC_{18}H_{37}){\cdot}H_2O^c$	5.7	48.5	4.9

[a] Bulk sample; refs 15, 16. [b] Bulk sample; ref 32. [c] LB film.

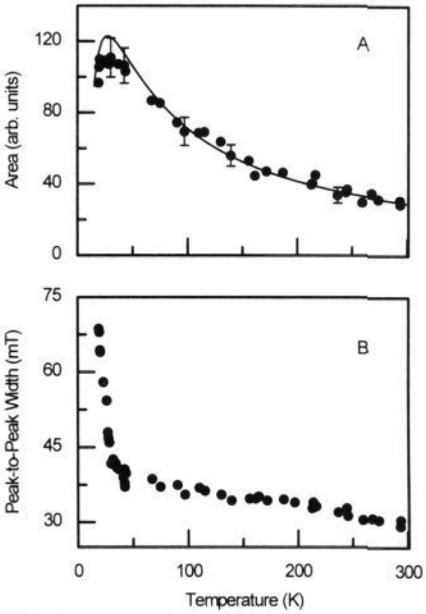

Figure 2. (A) The integrated area of the EPR signal as a function of temperature for a 50-bilayer film. The solid line is a fit to the data, according to eq. 1, for J/k = 3.0 K. (B) The EPR line width as a function of temperature for the same sample as in A. The sample is oriented with the magnetic field parallel to the LB plane.

A transition to long-range antiferromagnetic order is not observed in the EPR experiment. However, the data do show evidence for antiferromagnetic exchange and short-range order in a LB film. The observed magnetic exchange arises from the crystalline extended-lattice structure of the LB layers, and the magnetic behavior is nearly identical to that observed for bulk samples with similar in-plane structures. These systems should lead to meaningful comparisons of the magnetic behavior in single layers with the properties of known solid-state analogs.

Acknowledgment. We are grateful to Dr. Stephen. E. Nagler and Drew Garrett for the X-ray diffraction analysis and Dr. Augusto A. Morrone for the TED and TEM analyses. We would like to acknowledge the National Science Foundation (DMR-9205333) for financial support.

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