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Electron Paramagnetic Resonance Study of a Langmuir−Blodgett Film of Manganese Octadecylphosphonate and Comparison of the Magnetic Properties to Those of Solid-State Manganese Alkylphosphonates

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Langmuir−Blodgett (LB) films of manganese octadecylphosphonate ($Mn(O_3PC_{18}H_{37})\cdot H_2O$) are prepared by depositing octadecylphosphonate monolayers from a $MnCl_2\cdot 4H_2O$ containing subphase at a pH range of 5.2−5.6. Electron paramagnetic resonance (EPR) studies of the LB film give evidence for antiferromagnetic exchange in a two-dimensional inorganic extended lattice, in agreement with published magnetic studies of solid-state manganese alkylphosphonates. The g values of the LB film are characteristic of Mn^{2+} in a nearly cubic field and are essentially isotropic, ranging from 1.99 to 2.00. The dependence of the EPR line width on sample orientation in the magnetic field is consistent with the behavior predicted for a two-dimensional lattice with antiferromagnetic Heisenberg exchange. The temperature dependence of the integrated area of the EPR signal, which is proportional to spin susceptibility, is presented. A value for the antiferromagnetic exchange constant, J/k, of −2.8 K was determined for the LB film by fitting the data to a high temperature series expansion. This is in excellent agreement with the J/k values obtained for the solid-state manganese phosphonates. EPR line widths of both the manganese octadecylphosphonate LB film and a powder sample of manganese propylphosphonate increase rapidly as temperature is decreased below 30 K. This is characteristic of a system approaching a magnetic ordering transition and is caused by antiferromagnetic fluctuations. The solid-state manganese alkylphosphonates undergo antiferromagnetic ordering transitions at temperatures in the range 14.8−15.1 K, but an ordering transition in the LB film cannot be observed using EPR because the line width becomes too broad and the signal is too weak to measure below 17 K. The study confirms that the in-plane structure of the manganese phosphonate LB film is the same as that of the solid-state manganese phosphonate analogs.

Introduction

The layered nature of many solid-state metal phosphonates has attracted attention from researchers with a variety of interests. Solid-state structural studies have revealed several new layered structures for different combinations of metal ion and organophosphonate group.[1−8] The large internal surface areas in the solids, which result from the layered structures, suggest potential applications as catalyst supports and sorbents, and in sensing and separation applications.[3,9−11] The metal−phosphonate binding interaction has also been used in procedures to deposit monolayer and multilayer thin films.[12−22] The process deposits layers of functionalized organic molecules by alternately exposing a surface to solutions of metal ions and α,ω-disubstituted organophosphonic acids and has been used to prepare thin films for applications that require oriented assemblies of organic molecules.[12−15] In yet another area of interest, some of the transition metal phosphonates have been the subject of magnetic studies where the layered structures give rise to unusual magnetic properties and serve as useful models for investigating magnetic behavior in two-dimensional systems.[23−25]

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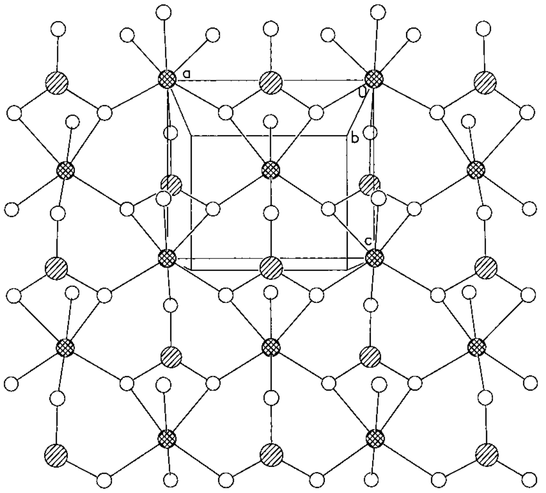


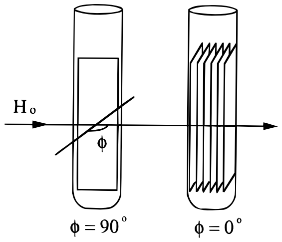
Figure 1. Structure of manganese phenylphosphonate, $Mn(O_3PC_6H_5)\cdot H_2O$ viewed down the *b* (stacking) axis. Phenyl groups were omitted for clarity. The powdered manganese alkylphosphonates are isostructural with the phenylphosphonate shown here. Structural data were taken from ref 26. Key: Cross-hatched circles, Mn; large diagonally shaded circles, P; small open circles, O.

Table 1. Structural and Magnetic Parameters for $Mn(O_3PR)\cdot H_2O$ Solids[a]

compound	*a*, Å	*b*, Å	*c*, Å	$-J/k$, K
$Mn(O_3PCH_3)\cdot H_2O$	5.82	8.82	4.90	2.70
$Mn(O_3PC_2H_5)\cdot H_2O$	5.83	10.24	4.87	2.78
$Mn(O_3PC_3H_7)\cdot H_2O$	5.84	11.71	4.91	2.48
$Mn(O_3PC_4H_9)\cdot H_2O$	5.84	14.72	4.91	2.48

[a] Reference 23.

Scheme 1. Orientations with Respect to the Magnetic Field, H_o, of the LB Film Stacked in a Conventional EPR Tube



Manganese organophosphonates crystallize in the orthorhombic space group P*mn*2$_1$. The crystal structure of $Mn(O_3PC_6H_5)\cdot H_2O$ reported by Cao et al.[26] nicely shows the layered nature of the solids and a view of the manganese phosphonate plane is reproduced in Figure 1.[26] The structure consists of layers of manganese ions, which are roughly co-planar, octahedrally coordinated by five phosphonate oxygens and one water of hydration. The phenyl groups are pointed away from the inorganic layer, approximately perpendicular to the manganese ion plane, and make van der Waals contacts between layers. The manganese alkyl phosphonates, $Mn(O_3PC_nH_{2n+1})\cdot H_2O$, have the same in-plane structure as the phenyl analog although the interlayer spacing varies as the alkyl group is changed.[23,26] Unit cell parameters for some manganese alkylphosphonates are given in Table 1.

Carling et al.[23] have performed static susceptibility measurements on powder samples of a series of manganese alkylphosphonates, $Mn(O_3PC_nH_{2n+1})\cdot H_2O$ ($n = 1-4$). The susceptibility as a function of temperature for each sample is characteristic of antiferromagnetic exchange in a low-dimensional lattice, and values of the nearest neighbor exchange, determined by Carling et al. from fitting the data to a model for a two-dimensional Heisenberg antiferromagnet, are listed in Table 1.[23] (In this paper we use the convention where the exchange constant, J, is defined according to the Hamiltonian, $H = -J\sum S_iS_j$, and a value of $J < 0$ indicates antiferromagnetic exchange.[27]) Each of the materials orders antiferromagnetically with ordering temperatures in the range 14.8−15.1 K.[23] Below the Néel temperature, T_N, the presence of a weak magnetic moment indicates that these materials are best described as canted antiferromagnets, which are also called "weak ferromagnets."[23]

Recently, we demonstrated that extended-lattice monolayers of some of the metal phosphonates could be prepared using Langmuir−Blodgett film deposition methods.[28,29] In the case of manganese octadecylphosphonate, it was shown using X-ray diffraction, XPS, and FTIR that the LB film has the same structure that is observed in several of the solid-state manganese alkylphosphonates.[28] In this paper, we report on a detailed EPR study of the manganese octadecylphosphonate LB film and compare the magnetic behavior of the LB film to published magnetism studies on the series of solid-state manganese alkylphosphonates.[23] The EPR results show that the LB film is well described as a two-dimensional lattice with nearest-neighbor Heisenberg antiferromagnetic exchange and that the magnitude of the exchange is the same as is seen in the solids. The EPR behavior confirms that the manganese phosphonate LB film is truly an extended-lattice structure. A preliminary account of part of this study was included in a previous communication.[28] The work presented here is a more thorough investigation of the EPR behavior of the manganese octadecylphosphonate LB film.

Experimental Section

Materials. Octadecylphosphonic acid, $C_{18}H_{37}PO_3H_2$, was used as purchased from Alfa Chemicals (Ward Hill, MA). Manganese chloride tetrahydrate, $MnCl_2\cdot 4H_2O$, was used as purchased from Fisher Scientific (Orlando, FL).

Instrumentation. Langmuir−Blodgett films were prepared using a KSV (Stratford, CT) 3000 Langmuir−Blodgett trough modified to operate with double barriers. Purified water having a resistivity of 18 MΩ cm was used. EPR spectra were recorded on a Bruker (Billerica, MA) ER 200D spectrometer modified with a digital signal channel and a digital field controller. Data were collected using a U.S. EPR (Clarksville, MD) SPEC300 data acquisition program and analyzed using a U.S. EPR EPRDAP data analysis program. Temperature was controlled using an Oxford Instruments (Witney, England) ITC 503 temperature controller and ESR 900 cryostat.

Procedure. Manganese octadecylphosphonate LB films were prepared by spreading octadecylphosphonic acid onto an aqueous subphase containing 5×10^{-4} M $MnCl_2\cdot 4H_2O$ held in a pH range of 5.2−5.6. The monolayer was compressed to a pressure of 17 mN/m and bilayers were transferred onto a 625 mm^2 calcium arachidate covered mylar substrate at speeds of 8 mm/min on the downstroke and 5 mm/min on the upstroke. Multilayers cannot be formed by continuous deposition of the film due to cross-linking of the phosphonate groups by the manganese ions at the air/water interface. After deposition of a bilayer, the monolayer was removed from the surface of the trough and a new octadecylphosphonic acid monolayer was formed. Films containing 50 bilayers were prepared, and transfer ratios were in the range 0.98−1.08. The mylar was cut into smaller strips and placed into an EPR tube.

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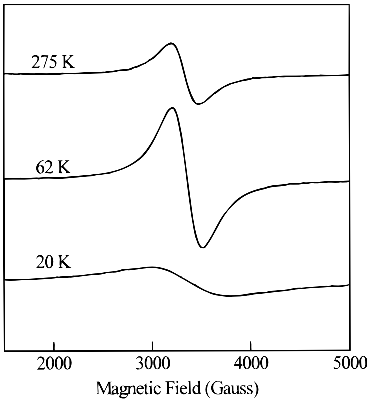

Figure 2. EPR spectra of the manganese octadecylphosphonate LB film at 275, 62, and 20 K. The sample was oriented with $\phi = 0°$ (Scheme 1). The EPR signal broadens substantially as the temperature is lowered below 30 K.

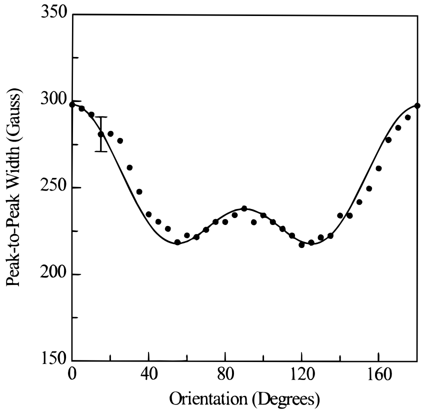

Figure 3. EPR line width as a function of sample orientation at room temperature. The sample orientation is defined in Scheme 1. The solid line is a fit to $\Delta H = A + B(3\cos^2\phi - 1)^2$ with $A = 218$ G and $B = 20$ G. The behavior is characteristic of a two-dimensional lattice with antiferromagnetic Heisenberg exchange.

Results and Discussion

Samples for EPR studies were deposited onto mylar sheets. After film deposition, the mylar was cut into thin strips that were stacked and placed in a conventional EPR tube. The oriented sample could then be rotated with respect to the magnetic field, as shown in Scheme 1. The LB film sample has a common *b* axis, with all the layers parallel to the substrate, but because the film is composed of ordered domains, the in-plane orientation (*ac* plane) is circularly averaged. The angle ϕ is defined as the angle between the film normal and the direction of the static field, as illustrated in Scheme 1.

Representative EPR signals of the LB film are shown in Figure 2. The signals for both the LB film and the solid-state samples are dipolar broadened, as expected for an exchange-coupled lattice, and no Mn^{2+} hyperfine splitting is observed. The *g* values are characteristic of Mn^{2+} in a nearly cubic field and are consistent with the *g* value of 1.99 observed for a powder sample of $Mn(O_3PC_3H_7)\cdot H_2O$. In contrast to the powdered solid-state samples, the LB films have a common *b*-axis orientation and the *g* values vary continuously as the sample is rotated with respect to the external field, although the values are nearly isotropic ranging from 1.99 to 2.00.

The room temperature EPR line width of the LB film is plotted as a function of sample orientation in Figure 3. Spectra were taken as the sample was rotated every 5° with respect to the magnetic field. The shape of the plot is consistent with the behavior predicted for a two-dimensional lattice with antiferromagnetic Heisenberg exchange.[30−34] For low-dimensional materials, the contribution to the line width originating from spin diffusion has a $(3\cos^2\phi - 1)^n$ dependence where $n = {}^4/_3$ for a one-dimensional lattice and $n = 2$ for a two-dimensional lattice.[30,32−34] The expected orientational dependence of the line width for a two-dimensional Heisenberg antiferromagnet is, therefore

$$\Delta H = A + B(3\cos^2\phi - 1)^2 \tag{1}$$

where *A* and *B* encompass exchange and other dipolar interaction terms.[32−34] A fit of the data with $A = 218$ G and $B = 20$ G is superimposed on the data in Figure 3. The line width has a minimum of 218 G at the magic angle $\phi = 54.7°$.

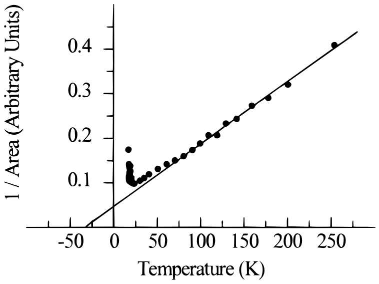

Figure 4. Temperature dependence of the inverse of the area (arbitrary units) of the EPR signal from the manganese octadecylphosphonate LB film. The solid line is a linear fit to the data above 80 K. An extrapolation of the high temperature data intercepts the temperature axis at −34 K, indicating antiferromagnetic exchange.

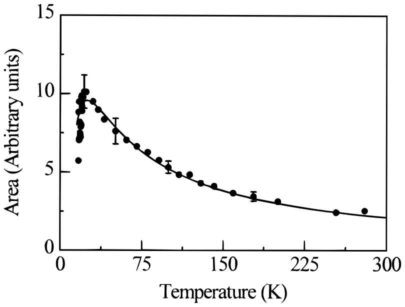

Figure 5. Temperature dependence of the integrated area (arbitrary units) of the EPR signal from the manganese octadecylphosphonate LB film. The solid line is a fit to the data using eq 2 for a two-dimensional lattice with Heisenberg antiferromagnetic exchange with exchange constant $J/k = -2.8$ K. Since the EPR intensity is plotted as arbitrary units, the fit has been fixed to the EPR intensity at 110 K.

The integrated area of the EPR signal is proportional to the spin susceptibility, and a plot of 1/area vs temperature is shown in Figure 4. An extrapolation of the high temperature data intercepts the temperature axis at −34 K indicating antiferromagnetic exchange. The data are also expressed in Figure 5 as area vs temperature. The area of the EPR signal gradually increases as the temperature is lowered and reaches a maximum near 25 K. The area then decreases rapidly until the EPR signal is lost around 17 K. The shape of the plot is characteristic of antiferromagnetic exchange in a low-dimensional solid,[30,31,35,36] and the behavior is nearly identical to the temperature dependent

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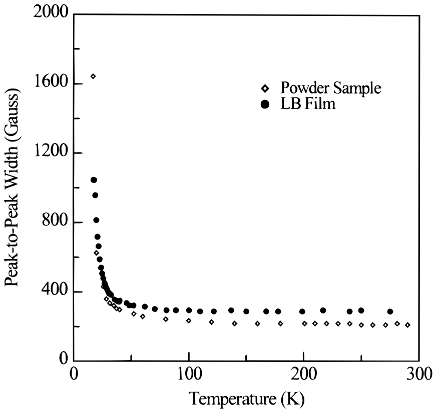

Figure 6. EPR line width as a function of temperature for a powder sample of manganese propylphosphonate and for the manganese octadecylphosphonate LB film. The rapid increase in line widths seen below 30 K is characteristic of systems approaching a magnetic ordering transition.

static susceptibility of the powdered solid-state manganese alkylphosphonates.[23]

Although there is no exact solution for the magnetic susceptibility, χ, of a quadratic-layer Heisenberg antiferromagnet, the temperature dependence can be described by a numerical series expansion[36]

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

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 nearest neighbor exchange constant. The coefficients, C_n, for $S = {}^5/_2$ have been calculated up to $n = 6$ by Lines.[35] The value of the exchange constant can be estimated by the temperature of maximum susceptibility, T_{max}, according to $kT_{max}/J = 2.06S(S + 1)$.[37] Taking T_{max} as 25 K yields $J/k = -2.8$ K and a fit to the data according to eq 2 is plotted as the solid line in Figure 5. Because the EPR intensity is plotted as arbitrary units, the fit has been fixed to the EPR intensity at 110 K. The value of the exchange constant, $J/k = -2.8$ K, agrees closely with the exchange constants for the bulk metal alkylphosphonates obtained by Carling et al.[23] and shown in Table 1. The fit of the EPR intensity to the numerical expression in eq 2 is further evidence that the LB film is a two-dimensional antiferromagnetic exchange-coupled lattice. The magnitude of the exchange is nearly identical to the solid-state analogs and suggests that the in-plane Mn−O−Mn interactions in the film are similar to those seen in the solid-state structures.

The peak-to-peak widths of the EPR signals of the manganese octadecylphosphonate LB film and a powder sample of manganese propylphosphonate are plotted as a function of temperature in Figure 6. In both cases the EPR line width remains approximately constant as the temperature is lowered below room temperature. As the temperature approaches 30 K, the line widths broaden rapidly until the signals become so broad they are lost below 17 K. The powder sample undergoes a magnetic ordering transition at $T_N = 14.90$ K to a canted antiferromagnetic state.[23] The increase in line width is characteristic of a system approaching a magnetic ordering transition and is caused by antiferromagnetic fluctuations. Large variations in the local field, caused by regions of short-range order fluctuating to achieve long-range order, result in the large line widths. The LB film also experiences antiferromagnetic fluctuations, although by EPR we cannot observe whether or not an ordering transition occurs because the signal becomes too broad.

Magnetic ordering is not predicted to occur in a truly two-dimensional Heisenberg lattice.[38−40] When ordering is observed in layered systems it occurs as a result of either anisotropy in the exchange or a dimensionality crossover in a temperature regime where the interlayer exchange, $J_\perp$, becomes important.[25,30,41] It is interesting to note that in the series $Mn(O_3PC_nH_{2n+1})\cdot H_2O$, where ordering does occur, dimensionality crossover has been observed to occur at values of the reduced temperature, $(T_N - T)/T_N$, of 0.085, 0.015, and 0.010 for $n =$ 2, 3, and 4, respectively.[25] For the LB films, interlayer exchange is not expected as the interlayer spacing is 48.5 Å. Also, as a result of the depositon process, layers are not in registry. The LB films should behave as isolated monolayers and dimensionality crossover should not occur.

The EPR behavior of the manganese phosphonate LB films can be compared to previous studies of magnetic exchange between metal ions in LB films. The most extensive studies are those of Pomerantz et al.[31,42−44] on LB films of manganese stearate. On the basis of line width analyses and temperature dependent EPR intensity data, antiferromagnetic exchange was also observed in the manganese stearate LB film and the value of the nearest-neighbor exchange was estimated as $J/k = -1.0 \pm 0.4$ K.[42] This value is smaller than the -2.8 K value for the manganese phosphonates and is related to differences in the in-plane structure of the two films. In the metal phosphonate film, in-plane bonding is well described by the structures of the known solid-state analogs. The manganese ions are nearly co-planar and each site is coordinated by five phosphonate oxygens and one water molecule. Adjacent manganese ions are bridged by a single phosphonate oxygen which mediates magnetic superexchange. The structure of the manganese stearate films is less clear.[43] The Mn^{2+} ions are certainly bridged by the carboxylate headgroups, but the mode of binding is not known. TED and AFM studies suggest a rectangular arrangement of Mn^{2+} ions.[45]

The observation of large shifts in resonance field at low temperatures was cited as evidence for spontaneous magnetization in the manganese stearate films.[46] Since the exchange is predominantly antiferromagnetic, the magnetic moment was attributed to canting of the antiferromagnetically ordered spins. However, direct observation of the ordered state has not been observed. An alternative explanation offered by Pomerantz[46] for the increased magnetization is the possibility of an antiferromagnetic lattice containing manganese ion vacancies, which cannot be discounted considering the LB film deposition method. The only evidence for ordering in the manganese phosphonate films is the large increase in line width at low temperature. As was discussed above, this is a precursor effect and is not itself evidence for ordering, although, the similarities in the behavior of the LB film and the powdered solids where

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ordering does occur are striking. It would be informative to study the magnetization of these films to lower temperature, but because of the limited sample size, the use of standard methods for measuring the static susceptibility has not yet been possible.

Conclusions

EPR studies of manganese octadecylphoshonate Langmuir–Blodgett films reveal that the magnetic exchange in the films is identical to that exhibited in solid-state manganese alkylphosphonates. The high temperature magnetic behavior (above T_N of the powders) for both the film and the solid-state materials is characteristic of antiferromagnetic Heisenberg exchange in a two-dimensional lattice. While the solid-state manganese alkylphosphonates order to form “weak ferromagnets”, direct observation of a transition to long-range order is not possible in the LB films using EPR. However, the EPR line width at low temperature is characteristic of a system approaching a magnetic ordering transition. Magnetization measurements are needed below 17 K to explore the ground state of the two-dimensional LB film.

The magnetic studies help confirm that the LB film has the same extended lattice structure as the solid-state alkylphosphonates. These results demonstrate that single layers of known solid-state layered structures can be prepared using LB methods. Since the inorganic lattice energy is the dominant interaction in the metal phosphonate layered structures, the possibility exists of using these structures to organize LB films of organophosphonates containing organic groups other than alkyl chains, in analogy to the known solid-state metal phosphonates based on functional organic groups.

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