from 3.3 to 3.8 Å, in steps of 0.1 Å. The minimum d spacing corresponds to the case where a Xe atom sits in a bridge (twofold symmetry) site. A constant inner potential $V_0 = 10$ eV is used for both the overlayer and substrate. The calculated IV curves were compared with the data of Webb and co-workers.[3,4] Figure 3 shows the comparisons for the (00) and (10) beams. From the comparison, we conclude that the optimal spacing is between 3.5 and 3.6 Å. We put it at 3.55 ± 0.1 Å. This result compares favorably to the result 3.5 $\pm$ 0.1 Å reported by Webb and co-workers.[3,4] Their result was obtained by data averaging over many incident angles.

It is apparent that the dynamical LEED approach may be appropriately modified to analyze surface structures of irrationally related lattices. It is probably due to the weak scattering power of Xe that we can completely neglect beam mixing terms in this work; however, because the theoretical method includes many more scattering events (third and higher orders for many events), we believe this procedure, with minor modifications, can adequately treat many of the stronger overlayer scatterers that are irrationally related to the substrate. In fact the importance of the beam mixing events can be estimated directly by inspection of the data prior to any calculation. The small peak at $\vec{g} + \vec{G}$ labeled "multiple scattering" in Fig. 4 of Ref. 4 results from such an event and such contributions to specular, overlayer, and substrate beams must be smaller than this peak by at least one order.

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[a] Also at Department of Physics, University of Wisconsin-Whitewater, Whitewater, Wisc.

[1] P. M. Marcus, *Characterization of Metal and Polymer Surfaces* (Academic, New York, 1977), Vol. 1, p. 271.

[2] P. M. Estrup and E. G. McRae, Surf. Sci. 25, 1 (1971).

[3] M. B. Webb and P. I. Cohen, CRC Solid State Sci. 6, 253 (1976).

[4] P. I. Cohen, J. Unguns, and M. B. Webb, Surf. Sci. 58, 429 (1976).

[5] M. A. Chesters, M. Hussain, and J. Pritchard, Surf. Sci. 35, 161 (1973).

[6] G. G. Kleiman and U. Landman, Phys. Rev. Lett. 31, 707 (1973), and Phys. Rev. B 12, 5484 (1973).

[7] J. P. Hobson, CRC Solid State Sci. 4, 221 (1974).

[8] N. Stoner, M. A. Van Hove, and S. Y. Tong, *Characterization of Metal and Polymer Surfaces* (Academic, New York, 1977), Vol. 1, p. 299.

Preparation of Literally Two-Dimensional Magnets

M. Pomerantz, F. H. Dacol, and Armin Segmüller
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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The Langmuir-Blodgett technique was used to deposit manganese stearate in the form of monolayers. Because of the nature of the method, and a variety of supporting experiments, it is concluded that the Mn atoms are arrayed on a single surface, thus forming literally two-dimensional magnetic materials.

There has been a great amount of theory of model magnetic systems in two spatial dimensions.[1] Experimental work to test the theories has also been extensive in recent years.[2] The experiments have, with one exception,[3] been done on materials that were three-dimensional, layer-like structures, and hence were "quasi two-dimensional." In these experiments the question remains of the influence of the third dimension. In this Letter we outline the preparation and characterization of *literally* two-dimensional (2-D) magnetic structures. Evidence for magnetic ordering at low temperatures will be published elsewhere.

We achieve exact two-dimensionality by depositing the magnetic materials in individual sheets that are one molecule thick. The method we used was an application of the well-known Langmuir-Blodgett technique.[4] Briefly, stearic acid, a long-chain fatty acid with formula HOOC-$(CH_2)_{16}$-CH_3, was spread on the surface of the water. The acidic "heads," HOOC ⋯, of these molecules tend to dissolve in water, releasing H^+; the fatty "tails," $(CH_2)_{16}$-CH_3, tend to float on the water [cf. Fig. 1(a)]. It is known that molecules spread in this fashion form a monolayer on the surface of the water. By dissolving 10^{-3} molar $MnCl_2$, the magnetic species, Mn^{2+}, had been previously introduced into the water and the pH was adjusted to 6.5–6.8 by gradual addition of dilute KOH. Under these conditions we found that a chemical reaction occurred in which Mn^{2+} became bonded ionically to the submerged COO^- ends of the molecules to form manganese stearate $Mn(C_{18}H_{35}O_2)_2$, (abbreviated as $MnSt_2$); these floated on the water as a monomolecular film. By this means we hope to catch a monolayer of Mn^{2+} ions on the ends of the organic molecules. The molecules were compacted and oriented with their lengths normal to the water surface by the application of a surface pressure of about 20 dyn/cm. The film was then lifted off the water by passing a solid substrate through the surface [cf. Fig. 1(a)]. In this first layer the molecules attach to hydrophilic substrates at their ionic ends [the Mn^{2+}-$(COO)^-_2$ group]. The magnetic Mn^{2+} ions in the first layer are thus in a literally two-dimensional array by construction. We shall refer to this as Structure I.

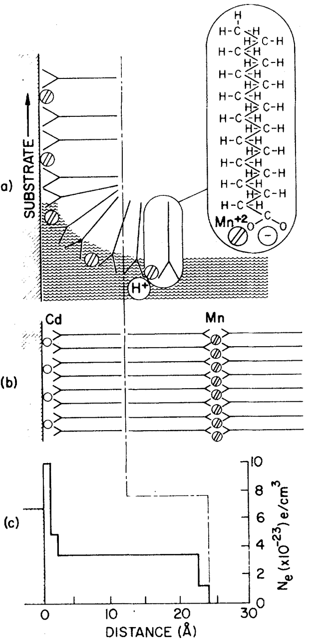

FIG. 1. (a) Schematic diagram of the deposition of a literally 2-D magnet by the Langmuir-Blodgett technique. The hydrophilic substrate (e.g., quartz) is pulled through the water surface. A monolayer of manganese stearate that was floating on the water adheres to the quartz to produce a "Structure I" film. The inset shows the structure of a stearate anion, and a Mn^{2+} ion. (b) Schematic cross section of a 2-D magnetic of structure II. The Mn ions are shown in a plane, but the actual structure may be nonplanar. (c) The electron density, N_e, as a function of distance used to calculate the x-ray diffraction for a single monolayer (Structure I magnet).

It proved possible to construct a second kind of 2-D magnetic structure by using triple dipping. This structure, which will be referred to as Structure II, was constructed by first coating the substrate with a monolayer of nonmagnetic cadmium stearate. (The method described above was used, except that cadmium ions were dissolved in the water.) Upon insertion of these coated slides into a second bath containing Mn ions, covered with a stearate monolayer, a $MnSt_2$ layer became attached to the $CdSt_2$ layer. The hydrocarbon tails of the $MnSt_2$ attached to the tails of the $CdSt_2$ layer. When the slide was pulled from the water a second layer of $MnSt_2$ was deposited, in which the $Mn^{2+}(OOC)^-_2$ head group of the new layer attached to the $Mn^{2+}(OOC\cdots)^-_2$ of the previous layer [cf. Fig. 1(b)]. It is possible that the Mn^{2+} ions of the two layers interleave to form a planar structure,[5] but the exact structure is not known at present. Whether planar or not, the Mn^{2+} ions are arrayed on a single surface which is two-dimensional.[6]

We have verified that Mn stearate films can actually be deposited as described above. A study using ESCA (electron spectroscopy for chemical analysis[7]) showed that Mn^{2+} is present in such samples. A full report of measurements using infrared (IR) absorption, electron diffraction, nuclear backscattering, and electron microprobe is in preparation.[8] In this Letter we will describe mostly x-ray diffraction and IR absorption, because these have been applied in new and revealing ways for the study of Langmuir-Blodgett films. We also present ESR result which confirm the two-dimensionality of the magnetic structure.

Structural studies.—It was known[9] that the x-ray diffraction from Langmuir-Blodgett films, in addition to the Bragg peaks, contains faint subsidiary maxima if the number of layers is small. We have used a highly monochromatic, well-collimated x-ray beam to observe this effect in detail[10] so that it can now be used to obtain semiquantitative information about the structure. In Fig. 2(a) for example, is shown the experimental diffraction from a single layer of $MnSt_2$ on a glass slide. There is a single interference maximum observed. We calculate the diffraction by a model,[14] shown in Fig. 1(c) for the structure based on the deposition process—that there are uniform layers of

Mn, OOC, $(CH_2)_{16}$, CH_3 repeated according to the number of films deposited. To calculate the x-ray diffraction one needs the corresponding electron densities and thicknesses of the layers. The parameters shown in Fig. 1(c) were derived from independent measurements of chemical densities and the known dimensions of the stearate molecule[12] and Mn^{2+} ion. A mean-square roughness[13] of 4.5 Å and tilting of the molecules,[5] found by fitting the data, were used as correction factors. The result of the calculation of the diffraction from a single-layer model, shown as the solid curve in Fig. 2(a), gives good quantitative agreement with experiment. Similarly good agreements were obtained for multiple layers. A nine-layer experiment and model calculation are shown in Fig. 2(b). We display the nine-layer result because the explanation of the richness of detail is a test of any proposed model. The x-ray diffraction thus confirms that planar layers of $MnSt_2$ in the expected number are present on the substrate.

Electron diffraction in transmission[8] showed a sharp-spot pattern corresponding to a monoclinic or orthorhombic unit cell with $a_0 = 5.0$ Å and $b_0 = 7.5$ Å. The packing is similar to that found in stearic acid[12] and lead stearate.[5] The crystallinity extended for at least tens of microns. We also observed broad-spot patterns indicative of strained monoclinic or hexagonal packing, which we attribute to poorly formed film.

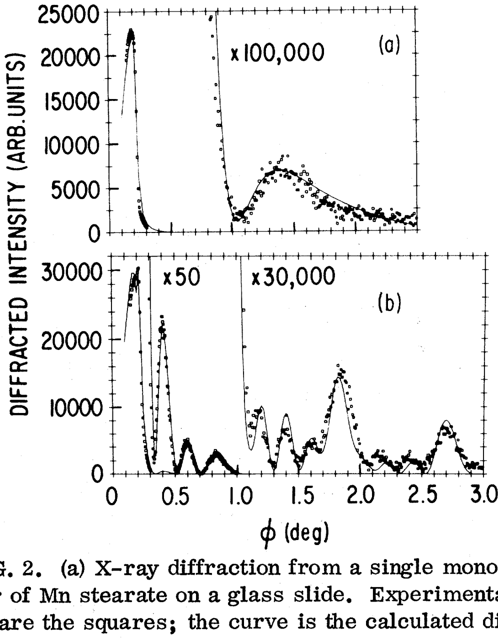

FIG. 2. (a) X-ray diffraction from a single monolayer of Mn stearate on a glass slide. Experimental data are the squares; the curve is the calculated diffraction from the model shown in Fig. 1(c). φ is the grazing angle. (b) X-ray diffraction from a nine-layer film of $MnSt_2$, similar to (a), except that a nine-layer model was used in the calculation.

Composition.—The presence of Mn chemically bound in the films was demonstrated by Hjortsberg, Chen, and Burstein[14] using a surface IR absorption technique. We deposited as few as two layers of $MnSt_2$ on Ag-coated glass slides. Prism coupling was used to launch a surface electromagnetic (SEM) wave along the metal film. The absorption was derived from the changes in reflectivity at excitation of SEM wave resonance, scanned in incident angle at fixed frequency. The observed spectrum of a particular sample has its strongest peak at 1435 cm^{-1}. This corresponds to the vibration of the COO^- group bound to Mn^{2+}, as observed in $MnSt_2$ powder.[15] A peak 30% as large was observed at 1720 cm^{-1} which is the known symmetric stretch frequency of the COOH group, i.e., unreacted stearic acid. Our conclusion is that Mn^{2+} has bonded to about 70% of the COO^- in this sample, which was made at pH 6.5. At higher pH more complete attachment of Mn to the COO^- can be achieved.[8]

It is possible that precipitates containing Mn might be deposited from the bath in addition to the $MnSt_2$ films. In some samples polycrystalline lines were observed in electron reflection diffraction. We determined by a number of tests that the amount of such contamination was small. For example, using electron microprobe we measured that the *total* Mn concentration on the substrates never exceeded the nominal stoichiometry of $MnSt_2$. The IR absorption[14] showed, however, that there is at least 70% conversion of stearic acid to $MnSt_2$. If there is no excess Mn, and most of the film is $MnSt_2$ there can be little Mn-bearing precipitate present. By careful sample-preparation technique it is possible to produce films in which no polycrystalline lines are found in the electron diffraction.[8]

2-D magnetism.—A clear demonstration that the Mn ions in our films are located in a 2-D arrangement is found in the ESR. A basic property of the 2-D structure is its shape anisotropy. This produces characteristic dipolar anisotropy effects in both the linewidths and line positions.[16] It has been observed in quasi 2-D magnets that the ESR linewidth is of the form $\Delta H \approx A + B(3\cos^2\vartheta - 1)^2$. The line positions have been observed to obey $H_0 = C + D(3\cos^2\vartheta - 1)$, where ϑ is the angle between the applied field and the normal to the film. Richards and Salamon[17] have given a theory of these angular dependences based on dipolar interactions in a 2-D array. Figure 3 shows our measurements of the ESR linewidth of a stack of Structure II films of $MnSt_2$. The characteristic angular dependence of a 2-D array is thus observed with $A = 220$ Oe and $B = 65$ Oe. The line positions, with a dipolar contribution of $D = 6 \pm 2$ Oe, at a frequency of 9.3 GHz at 80°K, also confirmed the 2-D arrangement of spins.

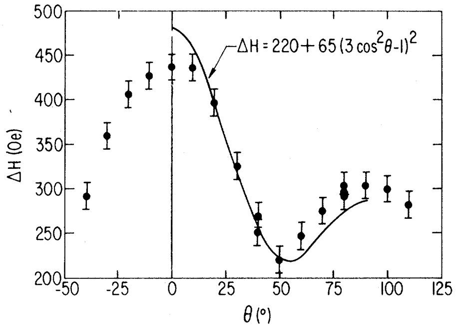

FIG. 3. The measured ESR linewidth, peak to peak of the derivative, of Structure II layers of manganese stearate as a function of θ, the angle between $\vec{H}_0$ and the film normal. The sample comprised fifty quartz plates, each with these layers, the plates being separated by 0.003-cm-thick bits of Mylar. The temperature was 80°K and the microwave frequency was 9.3 GHz. The solid curve is the form $H = A + B(3\cos^2\theta - 1)^2$ fitted to the data.

In summary, using the Langmuir-Blodgett technique we deposited monolayers of manganese stearate. In principle the Mn ions may be located in a single surface, forming a spatially two-dimensional array of magnetic ions. High-resolution x-ray diffraction confirmed the presence of layer structures. Surface IR wave absorption showed that the Mn was chemically bound in the expected position in the stearate molecules. The ESR of the films showed linewidth and position anisotropies characteristic of 2-D structures. The amount of Mn present as 3-D inclusions was shown to be small. It is also noteworthy that the films are quite stable. Under ordinary storage conditions, films have shown no noticeable deterioration in over two years.

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[1] Theory is reviewed in the series *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1972).

[2] Experiments are reviewed by L. J. de Jongh and A. R. Miedema, Adv. Phys. 23, 1 (1974).

[3] J. P. McTague and M. Nielsen, Phys. Rev. Lett. 37, 596 (1976).

[4] Reviewed in G. L. Gaines, *Insoluble Monolayers at Liquid-Gas Interfaces* (Interscience, New York, 1966).

[5] J. F. Stephens and C. Tuck-Lee, Appl. Crystallogr. 2, 1 (1969).

[6] The definition of the dimensionality of a lattice graph, $\dim L$, used by P. W. Kasteleyn [J. Math. Phys. (N.Y.) 4, 287 (1963)], $\dim L = 1 + \lim_{n\to\infty}(\ln N_n/\ln n)$, gives $\dim L = 2$ for a single surface of points even if it is not planar. N_n is the number of lattice sites whose shortest distance to a fixed site is n bonds of the lattice. Of course, we do not satisfy the mathematical or "thermodynamic" limit of $n \to \infty$.

[7] M. Pomerantz and R. A. Pollak, Chem. Phys. Lett. 31, 602 (1975).

[8] M. Pomerantz, E. Allessandrini, W. Hammer, S. Herd, and E. Simonyi, to be published.

[9] D. C. Bisset and J. Iball, Proc. Phys. Soc. London, Sect. A 67, 315 (1954).

[10] M. Pomerantz, F. H. Dacol, and A. Segmüller, Bull. Am. Phys. Soc. 20, 477 (1975), and to be published.

[11] A similar model has been used by W. Lesslauer, Acta Crystallogr B30, 1927 (1974).

[12] E. von Sydow, Acta Crystallogr. 8, 557 (1955).

[13] P. Croce and L. Nevot, J. App. Cryst. 7, 125 (1974).

[14] A. Hjortsberg, W. P. Chen, E. Burstein, and M. Pomerantz, Bull. Am. Phys. Soc. 22, 452 (1977), and to be published.

[15] Y. Koga and R. Matuura, Mem. Fac. Sci., Kyushu Univ., Ser. C 4, 1 (1961).

[16] ESR in quasi 2-D is reviewed by P. M. Richards, in Proceedings of the International School of Physics "Enrico Fermi", Course LIX, 1976 (to be published).

[17] P. M. Richards and M. B. Salamon, Phys. Rev. B 9, 32 (1974).