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Films of Mn₁₂-acetate deposited by low-energy laser ablation

J. Means^a, V. Meenakshi^a, R.V.A. Srivastava^a, W. Teizer^{a,*}, Al.A. Kolomenskii^a,
H.A. Schuessler^a, H. Zhao^b, K.R. Dunbar^b

^aDepartment of Physics, Texas A&M University, College Station, TX 77843-4242, USA

^bDepartment of Chemistry, Texas A&M University, College Station, TX 77843-3012, USA

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Abstract

Thin films of the molecular magnet Mn₁₂-acetate, [Mn₁₂O₁₂(CH₃COO)₁₆(H₂O)₄]·2CH₃COOH·4H₂O, have been prepared using a laser ablation technique with a nitrogen laser at low laser energies of 0.8 and 2 mJ. Chemical and magnetic characterizations show that the Mn₁₂-acetate cores remain intact and the films show similar magnetic properties to those of the parent molecular starting material. In addition, the magnetic data exhibit a peak in the magnetization at 27 K indicating the creation of an additional magnetic phase not noted in previous studies of crystalline phases.

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1. Introduction

A recent topic of great interest in materials science is that of single-molecule magnets, molecules which possess a large-spin ground state. These molecules have been fabricated and studied extensively [1]. One such molecular magnet is the Mn₁₂-acetate compound, first fabricated by Lis in

1980 [2]. The Mn₁₂-acetate molecule shows magnetic hysteresis at low temperatures due to slow paramagnetic relaxation [3,4]. The integration of these magnetic molecules into magnetic storage or nano-devices will require the successful production of thin films of the material. However, the thermal instability of the Mn₁₂-acetate compound renders standard thermal deposition techniques impractical. Films have been made using Langmuir–Blodgett techniques [5], as well as a few other methods [6–8], but we propose a simpler method, in line with more recent thin-film deposition technology.

*Corresponding author. Tel: +1-979-845-7730; fax: +1-979-845-2590.

E-mail address: teizer@tamu.edu (W. Teizer).

Pulsed laser deposition (PLD) has been used extensively for the deposition of organic and inorganic thin films [9]. In the present work, this technique is applied to produce films of Mn_{12} -acetate which mostly maintain the magnetic and molecular properties of the crystalline starting material.

Previously, some of us have performed laser ablation of Mn_{12} -acetate samples with an excimer laser with energies ranging from 200 to 450 mJ [10,11]. Films formed with the excimer laser were found to show partial fragmentation in the Mn_{12} -acetate molecules at high laser energies. Lowering the laser energy was shown to reduce the fragmentation. In the present study we used a nitrogen laser that ablated Mn_{12} -acetate at much lower pulse energy.

2. Experimental

In preparation for the laser ablation, the crystalline starting material was pressed into a pellet at a pressure of $\sim 19,000$ Torr. The pellet was then mounted as an ablation target in a high vacuum chamber ($P \approx 5 \times 10^{-6}$ Torr), where substrates (typically glass, mica or Si/SiO_2) were mounted at a distance of about 5 cm from the target. Films were fabricated using two different settings: (1) a pulse frequency of 8 Hz at an energy of 0.8 mJ for 5.5 h, and (2) a pulse frequency of 20 Hz with an energy of 2 mJ for 3 h. The resulting films were then characterized using X-ray photoelectron spectroscopy (XPS) and superconducting quantum interference device (SQUID) magnetometry in order to test if the Mn_{12} -acetate molecules remained intact and therefore retained their inherent molecular magnetic properties.

3. Results and discussion

Chemical characterization of the films was carried out using XPS. Figs. 1–3 show the XPS data for the Mn 2p, O 1s, and C 1s peaks, respectively, in the starting material and in films created using the two different sets of conditions mentioned above. All data were normalized to a

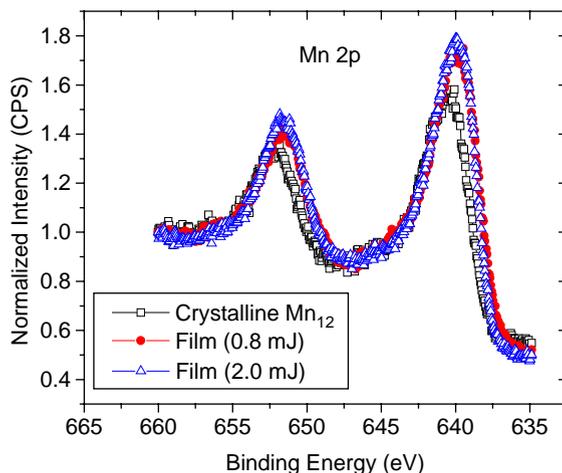


Fig. 1. XPS spectrum showing the binding energy peaks for the Mn 2p orbitals in the Mn_{12} -acetate starting material and two ablated films (one created at 8 Hz, 0.8 mJ, and the other at 20 Hz, 2.0 mJ), normalized to 1 at the highest binding energy.

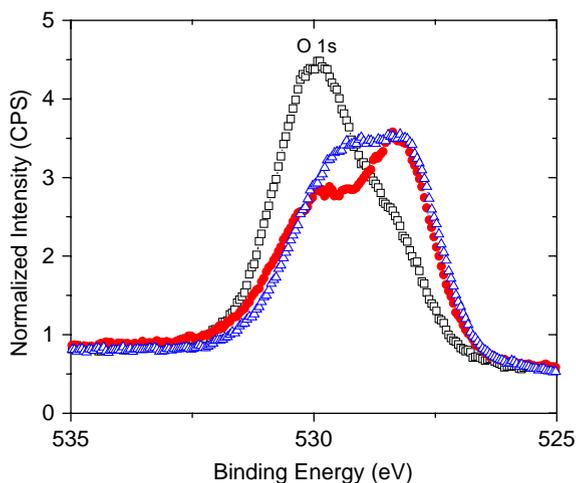


Fig. 2. XPS spectrum showing the binding energy peaks for the O 1s orbitals in the Mn_{12} -acetate starting material and two ablated films (one created at 8 Hz, 0.8 mJ, and the other at 20 Hz, 2.0 mJ), normalized to 1 at the highest binding energy. See Fig. 1 for key to symbols.

value of 1 at the highest energy. In Fig. 1, we note that the peak positions for Mn have changed very little. The Mn 2p peaks at 652.0 and 640.2 eV correspond to the $2p_{1/2}$ and $2p_{3/2}$ core levels, respectively. These are in reasonable agreement

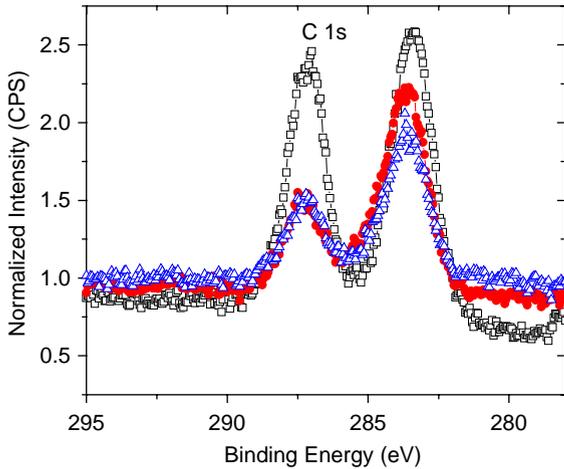


Fig. 3. XPS spectrum showing the binding energy peaks for the C 1s orbitals in the Mn_{12} -acetate starting material and two ablated films (one created at 8 Hz, 0.8 mJ, and the other at 20 Hz, 2.0 mJ), normalized to 1 at the highest binding energy. See Fig. 1 for key to symbols.

with the values found by Kang et al. using photoemission spectroscopy [12]. The shift of the Mn 2p peak positions in the ablated samples relative to those in the starting material range from 0.5 to 0.7 eV. The experimental resolution of ~ 0.5 eV indicates that these shifts could be due to a small change in the binding state of the manganese atoms within the film. These shifts are consistent with a change in the magnetic properties, as will be discussed below.

In Fig. 2, it should be noted that the starting material shows two oxygen peaks (one appears as a shoulder on the right). These correspond to the oxygen atoms which are bonded to the manganese ions in the core of the Mn_{12} -acetate molecule (528.1 eV) and to the oxygen atoms contained in acetate and water ligands (529.9 eV) surrounding the core. These values are also in reasonable agreement with those given by Kang et al. [12]. Small variations might be attributed to charging effects due to the insulating nature of the samples. There is a shift in the relative intensity of the two peaks in the ablated material versus that of the starting material. In the original Mn_{12} -acetate compound, the integrated area of the peak from the oxygen atoms in the core is significantly

smaller than that of the other peak. In the ablated samples, the area of the higher-energy peak is roughly equal to or lower than that of the other peak. This may indicate a reduction in the amount of oxygen from the water and acetate ligands, as could be the case if some of the ligands are being lost in the ablation process.

Fig. 3 shows two carbon peaks in the XPS data for the crystalline starting material. The two peaks, with binding energies of 283.3 and 287.1 eV, arise from the two carbon atoms in the acetate ligand [12]. A reduction in intensity in both of these peaks in the ablated films gives further indication that some acetate ligands may be lost in the ablation process. All of the XPS data taken together provide evidence that the manganese cores remain intact while some of the acetate ligands are lost in the ablation. Since the molecular magnetic properties result primarily from the core, this conclusion would be supported by the retention of the major magnetic features of the material, as shown below. This is a central issue in this study. Furthermore, we note that the loss of acetate ligands could permit an enhanced interaction between neighboring molecules and thus be responsible for the formation of an additional magnetic phase with a higher blocking temperature, as may be observed below. It should be noted that, while the given values for the XPS peak positions may show small variations from those previously reported in the literature, comparison of the values found for the films to those of the starting material are in close agreement.

Magnetic characterization was performed using SQUID magnetometry. In the Mn_{12} -acetate starting material, a strong hysteresis was observed in the magnetization data at low temperature, indicating a locking of the magnetic state as reported earlier [3] (not shown). Also of note were steps in the hysteresis, which indicate the presence of quantum tunneling of the magnetization [13,14]. Fig. 4 shows the magnetization, M , as a function of the applied field, B , at temperature $T = 1.8$ K for Mn_{12} -acetate which was ablated at 8 Hz and 0.8 mJ and subsequently scraped from the substrate. This sample exhibits hysteretic behavior. The reason for the narrowing of the hysteresis as compared to that of the starting material is the

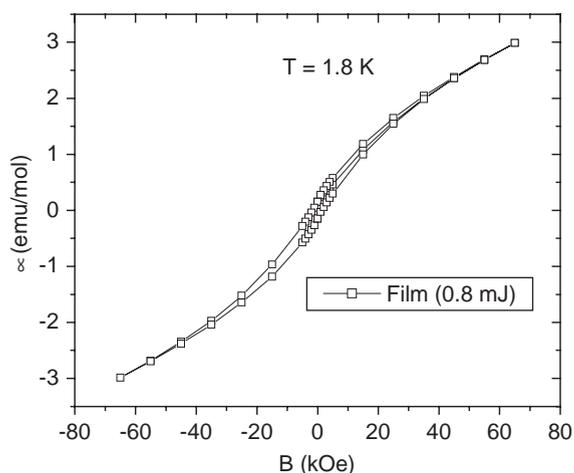


Fig. 4. Magnetization as a function of applied magnetic field for the ablated material at a temperature of 1.8 K, showing hysteresis.

random orientation of the molecules in the ablated material [5,13]. Consistent with prior results (Fig. 3 in Ref. [5]), we do not observe the customary resonant tunneling steps, which is also attributed to orientational disorder in the thin films. The crystalline structure of the starting material leads to more defined features. The mere presence of hysteresis, however, argues that there is superparamagnetic blocking of the magnetization below 3 K.

Fig. 5 shows the magnetic moment of the ablated material in a field of 50 Oe as a function of temperature for the same sample cooled at zero-field and cooled at a field of 50 Oe. In the zero-field cooled curve, we see a peak at $T = \sim 2.2$ K (see inset, Fig. 5) which corresponds to the onset of superparamagnetic behavior. This peak is normally observed at 3.0 K in crystalline Mn_{12} , but this temperature has been found to depend on whether the material is a single crystal or polycrystalline [2,15]. The presence of some other minority magnetic species can also cause a shift in the blocking temperature [16]. In addition to the peak at 2.2 K, a maximum was observed at $T = \sim 27$ K. This extra peak may result from the formation of an additional magnetic phase during the ablation process. This new phase causes the material to undergo a second transition with a

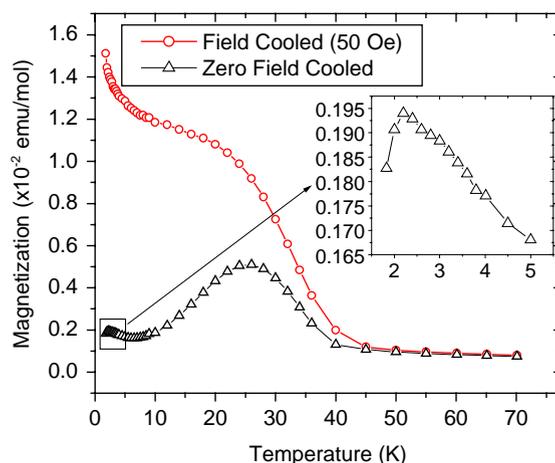


Fig. 5. Magnetic moment as a function of temperature for the ablated material in a field of 50 Oe with cooling in zero-field and in a field of 50 Oe. The insert shows the low-temperature region of the zero-field cooled data.

higher blocking temperature than that of the individual molecules. We propose three possible explanations for the additional phase: (1) it could arise from the formation of clusters of linked molecules; (2) it could be the result of a surface effect wherein interactions with the substrate alter the anisotropy of the molecules; or (3) it could be the result of the creation of a spin-glass state within the material. Any of these processes would be consistent with the removal of acetate ligands (as indicated by the XPS data) and thus a stronger interaction between the Mn_{12} -acetate core and its immediate environment.

4. Conclusion

This study has shown that nitrogen laser ablation is a viable technique for the creation of thin films of Mn_{12} -acetate. XPS data are consistent with the conclusion that, while some of the surrounding acetate ligands and water molecules are removed in the ablation process, the cores of the molecules remain intact. Magnetic measurements support this conclusion, with a blocking temperature in the 2–3 K range along with the characteristic hysteresis. There is also evidence of

an additional magnetic phase that has not been observed in previous studies of crystalline Mn_{12} -acetate.

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