Spin-glass behavior in $CoSt_2$ Langmuir-Blodgett multilayer films

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The dc susceptibilities have been measured on cobalt stearate ($CoSt_2$) Langmuir-Blodgett (LB) multilayer films. Two successive peaks and irreversibility are observed clearly in both parallel and perpendicular directions to the *c* axis. These behaviors are consistent with the mean-field theory for the Heisenberg-type spin-glass system having a weak single-ion anisotropy. The above behavior has never been observed in small $CoSt_2$ particles, so it is considered to be an inherent characteristic in the LB film structure. The magnetic behaviors between $CoSt_2$ LB films and other related compounds are compared and discussed. [S0163-1829(99)03142-2]

Recently, molecular-based magnets have attracted significant attention as materials with novel physics.[1] On the other hand, theoretical and experimental activity in the study of low-dimensional magnetism has focused on the role of dimensionality on the magnetic behavior near phase transitions.[2] The Langmuir-Blodgett (LB) films with magnetic ions offer unique opportunities for studying low-dimensional magnets, i.e., testing different theoretical models of order (or disorder) in two-dimensional (2D) magnets.[3] Some attempts have been made to study 2D magnetism.[4,5] The results have manifested the existence of an antiferromagnetic interaction within layers of manganese stearate ($MnSt_2$) which is the most studied case, with Néel point $T_N \leqslant 10\,K$.[6] The $MnSt_2$ was therefore considered to be the best example of a Heisenberg interaction among the transition-metal ions. The other transition-metal stearates and other carboxylates (but not LB films) were examined to search for other materials that might undergo magnetic order.[7] The only one that showed signs of ordering was ferric stearate.[8] In this study we describe experiments that suggest the possible existence of spin-glass behavior in cobalt stearate ($CoSt_2$) LB multilayer films.

The 119-layer LB film of $CoSt_2$ was prepared with a standard LB method. The stearic acid was dissolved in *n*-hexane (5.0×10^{-4} M). The solution was spread on a Milli-Q purified water subphase containing $CoCl_2$ in a concentration of 1.0×10^{-3} M, adjusted at *p*H 5.8 with $NaHCO_3$. The film was deposited (*Y*-type) onto a quartz substrate at a constant surface pressure (20 mN/m) and at the temperature of 20 °C. The crystallographic axes were determined from x-ray analysis. Magnetic measurements were carried out with a superconducting quantum interference device magnetometer (Quantum Design MPMSR2). The temperature dependence of the field-cooled (FC) and the zero-field-cooled (ZFC) susceptibilities was measured at temperatures between 1.5 and 100 K by applying a magnetic field parallel and perpendicular to the *c* axis. The experimental procedure was as follows. The sample was cooled in zero field to 1.5 K, a field H ($0 \leqslant H \leqslant 100$ Oe) was applied and the ZFC susceptibility was measured up to 100 K. Then, without changing the field, the sample was cooled to 1.5 K and the FC susceptibility was measured.

Figure 1 shows the x-ray-diffraction pattern of 119-layer $CoSt_2$ LB film. A series of equidistant diffraction peaks is shown in the figure, demonstrating the periodic structure of the film. The second-, fourth-, and sixth-order weakening phenomenon of the peak intensity appears due to the well-ordered assembly of the hydrocarbon chains, which is considered to be a typical feature of the x-ray-diffraction patterns of LB films.[9] The long spacing of LB film is related to the d_{00l} value of the corresponding peak as $d = l d_{00l}$. By substituting the d_{00l} value into the above equation, the long spacing of $CoSt_2$ LB film is obtained as 50.0 ± 0.1 Å. According to the chain length of the $CoSt_2$ monomolecule, the repeating unit in the film is bilayer. It is known that the x-ray-diffraction measurements can be applied not only to study ordered assembly structure and the long spacing of $CoSt_2$ LB films, but also to evaluate the orientation of the hydrocarbon chain axis.[10] It was concluded that the long spacing of multilayer stearate salts LB films of ca. 50 Å indicates the vertical orientation of chain axis to film surface.[10] Associated with this, the hydrocarbon chains in the $CoSt_2$ LB film are understood to be packed parallel to each other in a hexagonal unit cell with all-trans conformation.

Figure 2 exhibits the ZFC and the FC susceptibility branches (open and full symbols, respectively) of the $CoSt_2$

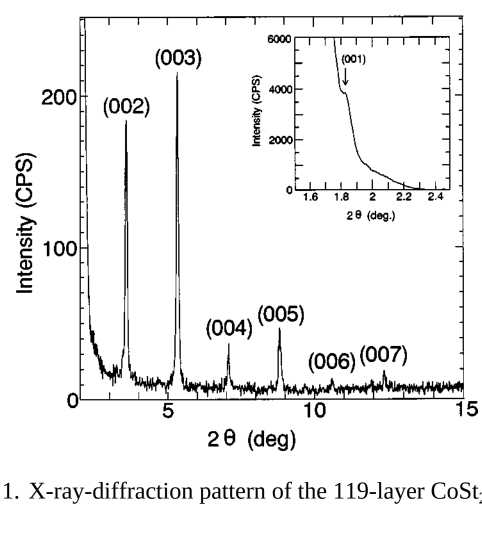

FIG. 1. X-ray-diffraction pattern of the 119-layer $CoSt_2$ LB film.

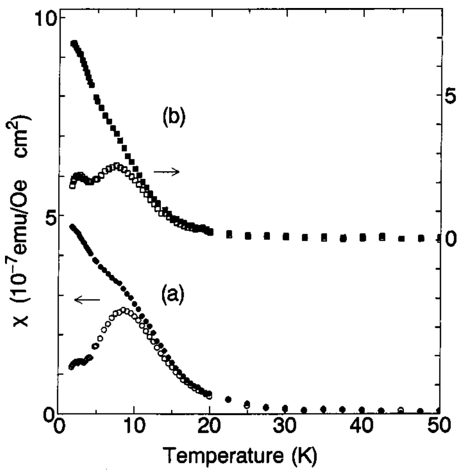

FIG. 2. Temperature dependence of the FC and the ZFC susceptibilities of $CoSt_2$ LB film, in a field $H=100$ Oe (a) parallel and (b) perpendicular to the c axis. Open and full symbols represent the ZFC and the FC branches, respectively. The curves (a) and (b) have been offset for clarity.

LB film measured with a field $H=100$ Oe in the temperature range 1.5–50 K. The circles and squares represent data taken with field H parallel to the c axis ($\chi_{\parallel}$) and perpendicular to the c axis ($\chi_{\perp}$), respectively. Our study reveals three main features of the magnetic susceptibility of the $CoSt_2$ LB film. (i) At low temperature, the longitudinal ($\chi_{\parallel}$) and the transverse ($\chi_{\perp}$) susceptibilities deviate significantly from a paramagnetic behavior and exhibit two clear successive peaks. (ii) Irreversibility, characterized by the difference between the FC and the ZFC branches and characteristic of a spin-glass order, is found already above the temperature at which the higher temperature peak appears. (iii) The intensity of the lower temperature peak depends strongly on the directions of applied magnetic field. It increases significantly as the applied field is perpendicular to the c axis. The occurrence of two successive peaks in both directions obviously suggests that the longitudinal and transverse components of Co spins freeze independently. Moreover, the enhancement of the intensity of the lower temperature peak for the applied field perpendicular to the c axis indicates that the lower temperature peak can result from the freezing of the perpendicular components. The high sensitivity of the lower temperature peak to the directions of applied magnetic field suggests that the system has a low-dimensional character and that the spin easy axis is along the c axis. The above features remind us of the scenario of two successive spin-glass transitions.[11–13]

Magnetic properties of spin glasses with single-ion uniaxial anisotropy have been extensively studied.[14,15] It is known that in a Heisenberg-type spin-glass system with a weak single-ion anisotropy, regardless of the type of crystal-field anisotropy $D>0$ (Ising type) or $D<0$ (planar type), the components parallel to the spin easy axis freeze first and the perpendicular components freeze subsequently. We consider that a weak but definite Ising-type anisotropy in $CoSt_2$ LB film causes spin-glass freezing of the components parallel to the c axis first at a higher temperature and then that of the remaining components perpendicular to the c axis at a lower temperature. The existence of the spin easy axis along the c axis is similar to the case of $MnSt_2$.[16] The second transition

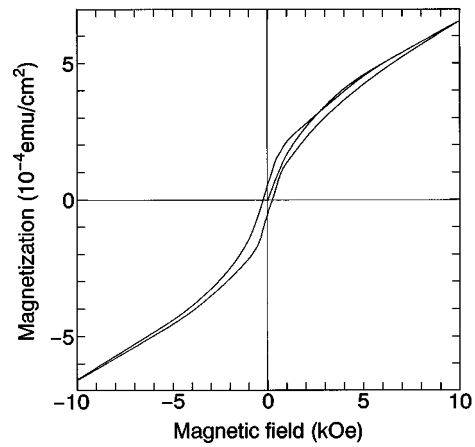

FIG. 3. Hysteresis loop at 4.2 K for $CoSt_2$ LB film.

does not exist for sufficiently strong anisotropy D.[11] Also, we note that the higher temperature peak occurs at the different temperatures ($\Delta T \simeq 1$ K) in $\chi_{\perp}$ and $\chi_{\parallel}$. This indicates that the induced components of Co spins parallel to the c axis order dependent on the direction of the applied field.

The hysteresis loop of $CoSt_2$ LB film at 4.2 K, after zero-field cooling, is presented in Fig. 3. The loop is narrow and shows a low remanent magnetization compared to the saturation. Such magnetic properties have their origin in the existence of a long-range antiferromagnetic interaction associated with some disorder.[17] It should be noted that a hexagonal 2D antiferromagnetic system is frustrated.[18]

Figure 4 shows the time dependence of the thermoremanent magnetization for $CoSt_2$ LB film at 4.15 K, field-cooled in 1 kOe. We find that the curve is best fitted by $M(t) = M_0 - S \ln t$, where $M_0 = 6.99\times 10^{-5}$ emu/cm^2 and $S = -3.29\times 10^{-6}$ emu/cm^2. Such a slow relaxation to a change in magnetic field is a typical phenomenon found in many spin glasses.[19]

In order to check whether the observed behavior can be due to the existence of 3D $CoSt_2$ inclusions in the multilayer structure, we have measured the temperature dependence of the ZFC susceptibility of cobalt stearate powder (Fig. 5). It is

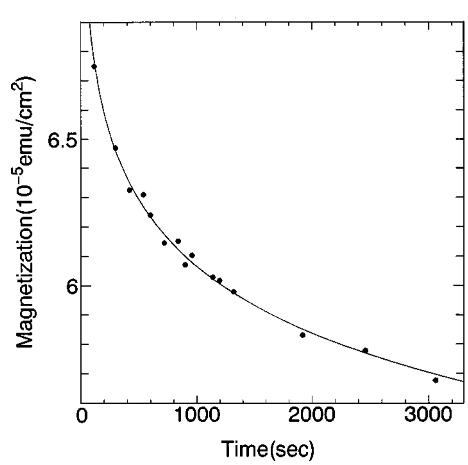

FIG. 4. Time dependence of the thermoremanent magnetization for $CoSt_2$ LB film. The solid line is the best fit of $M(t) = M_0 - S \ln t$ to the data, where $M_0 = 6.99\times 10^{-5}$ emu/cm^2 and $S = -3.29\times 10^{-6}$ emu/cm^2.

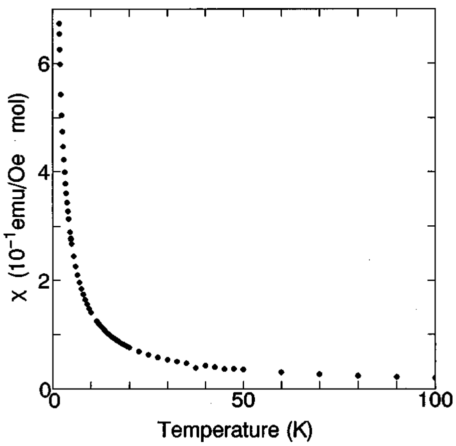

FIG. 5. Temperature dependence of the ZFC susceptibility of $CoSt_2$ powder.

found that $CoSt_2$ powder sample shows a qualitatively different susceptibility behavior from that of $CoSt_2$ LB film. It seems thus inconceivable that 3D inclusions of $CoSt_2$ in the LB film structure cause the spin-glass behavior observed. Previous absorption Mössbauer spectroscopy measurements showed no significant difference between iron arachidate LB films and small iron arachidate particles.[20] This conclusion was expected, because the two-dimensional structure is mainly preserved in the small ''LB particles.'' Our result is distinctly different from that of the above measurements.

It is interesting to compare our system to other related compounds. Among them, intercalation of magnetic spiecies in graphite provides a very useful system for the study of 2D magnetism.[21] In these systems, the interplanar interaction or magnetic moments can be systematically reduced by inserting a controlled number n of diamagnetic graphite layers between each adjacent pair of magnetic intercalate layers. The number n is called the stage of the graphite intercalation compound. The stage dependence of the magnetic susceptibility of stage -2, -4, -5 $CoCl_2$ graphite intercalation compounds (GIC's) was investigated.[22] The susceptibility anomaly consisted of two closely spaced peaks which are separated by a local minimum. The plot of the double-peak temperature separation as a function of stage for the in-plane susceptibility displayed a monotonic increase of the peak separation with increasing stage. We can estimate the value of temperature separation, $\Delta T \simeq 2$ K, by extrapolating the plot to the distance of 50 Å for $CoSt_2$ LB film, which is much smaller than that ($\Delta T \simeq 6$ K) observed. Moreover, in $CoCl_2$ GIC, the temperature ($T \simeq 7-8$ K) of the lower temperature susceptibility peak is relatively independent of stage and is much higher, compared to that ($T = 2$ K) observed in this study. The Co GIC was also found to exhibit a spin-glass behavior at low temperature;[17] however, it showed a single peak. It was reported that a spin-glass transition occurs also in the magnetic susceptibility of $CoCl_2 \cdot H_2O$.[23] But in this case, a weak and broad maximuim occurs in the 6–7 K range and irreversibility disappears above 7 K, which is much lower compared to our case ($T \simeq 18$ K). Moreover, the time dependence of the thermoremanent magnetization was represented by the product of algebraic and stretched exponential dependences, not by a logarithmic form which accounts for the decay in our case. Hence the mechanisms behind the behaviors in the above compounds may not explain our result in a straightforward way.

In summary, we have measured dc susceptibilities on $CoSt_2$ LB multilayer films. The ZFC curves with pronounced two maxima, irreversibility, the shape of the hysteresis loop and the time dependence of the thermoremanent magnetization are indications of spin-glass behavior. In both directions, two successive peaks are observed clearly and the intensity of the lower temperature peak enhances significantly for the applied magnetic field perpendicular to the c axis. The results indicate that the spin components parallel to the c axis freeze first and then the remaining components perpendicular to the c axis freeze at a lower temperature, being consistent with the theory on the Heisenberg-type spin-glass system having a weak single-ion anisotropy. At this point of our investigation, the following points remain to be elucidated in this system: (i) What competing interactions are responsible for the spin-glass behavior? (ii) Is this system two or three dimensional (independently of the well established two-dimensional crystallographic structure)? While the origin of the phenomenon observed is as yet unclear, the mode of the preparation (i.e., the LB method) suggests that the $CoSt_2$ film may well exhibit significant magnetic ion site randomness or defect concentration as well as frustration and low dimensionality of magnetic interactions. Further experiments, especially neutron-diffraction measurements, will give us useful information about the type of magnetic structure and exchange interactions.

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