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Magnetic and Magneto-topical Properties of RMn_6Sn_6 Single Crystals where $R = \text{Gd, Tb, Dy, Ho, Er, Tm, Lu}$

by

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1. INTRODUCTION

1.1. Rationale

Considerable work has been done recently on the study of magneto-optical materials. It has been motivated mainly by a search for materials with large Kerr rotations for use in magneto-optical information storage. Several of these devices are commercially available; however, the materials used for the recording media are less than optimal, and thus there is an interest in improving these materials. Previous work has yet to provide a rule of thumb for obtaining improved magneto-optical response. One class of materials that have shown some promise are those which contain manganese. Some examples include MnBi, MnBiAl, $R_x\text{MnBi}$, MnSb, and PtMnSb.

This provided the rationale for a literature search of ternary compounds containing manganese, a rare earth element, and an arbitrary third element. This list of compounds was then narrowed to include only compounds which are known to order above room temperature. From this shorter list, the series RMn_6Sn_6 (where R is one of the rare earth elements) was selected because it formed with a large number of rare earth elements and thus allowed a systematic study of a series of compounds to be performed. By studying trends as the lanthanide element is varied, it was hoped that some insight into the magnetic and magneto-optical properties could be found.

1.2. Lanthanides

The lanthanides consist of 15 elements, from lanthanum to lutetium, which all occupy a single location on the periodic table. These elements have a similar electron configuration, differing only in the number of 4f electrons. It can be written generally as $[\text{Xe}]5d^1 4f^n 6s^2$, where [Xe] is the closed shell configuration for xenon, and n ranges from 0 for lanthanum to 14 for lutetium. Energetically, the 4f electron levels lie below those of the 5d and 6s electrons and generally do not become involved in the chemical bonding. This leaves the 3 electrons which are located in the 5d and 6s orbitals as the valance electrons.

One interesting result of this electron configuration is the lanthanide contraction. It has been experimentally found through comparisons of the lattice parameters in isostructural series of lanthanide compounds that the radii of the lanthanides decrease in a regular and smooth fashion from lanthanum to lutetium. This is explained by the fact that the 4f electrons do not effectively screen the outer electrons from the increased nuclear charge as an additional 4f electron is added in moving from one lanthanide to the next [1].

Aside from the lanthanide contraction, other properties often exhibit a regular and systematic variation across the series of lanthanides. The use of systematics has been an important tool in understanding the rare earth elements. For example, the anomalous atomic volumes of metallic europium and ytterbium were found to be evidence of their divalent nature [1]. Systematics have also been used to show that 4f hybridization with the valence electrons occurs in both the pure metals and in alloys [2]. The creation of a generalized phase diagram for all the intra-rare earth binary alloys is another powerful tool that is made possible by the systematics in the lanthanide series of elements [3].

1.3. Magneto-optics

The term “magneto-optic effect” is used to describe the processes by which the axis of polarization of a linearly polarized light beam is rotated by a magnetized material. One magneto-optic phenomena is the Faraday effect where the polarization of a light beam is rotated as it is transmitted through a material. In the Kerr effect, the rotation occurs when the light beam is reflected from the surface of a material. The Kerr effect can be measured in three different configurations, comprising the polar, longitudinal, and equatorial Kerr effects. In the polar Kerr effect, the magnetization is perpendicular to the reflecting surface. In the longitudinal Kerr effect, the magnetization is parallel to the reflecting surface and parallel to the plane of incidence. In the third variation, the equatorial Kerr effect, the magnetization is parallel to the reflecting surface and perpendicular to the plane of incidence [4].

1.3.1. Phenomenological Models

The rotation of the plane of polarization caused by the Faraday Effect in a paramagnetic material can be given by

$$\theta = VHt,$$

where V is the Verdet constant, H is the field strength, and t is the path length of light in the material. For ferromagnetic or ferrimagnetic materials a similar equation can be written

$$\theta = KMt,$$

where the Verdet constant has been replaced by K , Kundt's constant, and the field strength has been replaced by the magnetization M .

For the Kerr effect, the rotation of the plane of polarization after reflection from a magnetized medium is given by

$$\theta = K_r M [5].$$

The above equations make no attempt to explain the origin of the magneto-optical properties of a material, but rather lump all this information into a materials constant. It should be noted that these materials constants are not actually constant, but rather depend on the wavelength of the incident radiation.

1.3.2. Microscopic Models - Interband Transition Effects

In a non-magnetic material, the microscopic origin of both the Faraday effect and polar magneto-optical Kerr effect is the Zeeman splitting of the atomic levels on application of a magnetic field. The different selection rules for right and left circularly polarized light lead to a splitting of the absorption and dispersion curves for the two states of polarization. The magneto-optical signals in ferromagnetic and ferrimagnetic materials tend to be several orders of magnitude greater than those in non-magnetic materials. This is explained by the spin-orbit splitting that occurs in ferromagnets. The spin-orbit interaction couples the magnetic moment of the electron with the magnetic field that the electron sees when it moves with a certain momentum through the electric field inside the medium. Further analysis shows that the important parameters for

obtaining a large Kerr effect include: the spin-orbit splitting, the joint spin polarization, the number of occupied initial states just below the Fermi energy, and the number of empty final states [6].

1.3.3. Microscopic Models - Intraband Transition Effects

Metals and doped semiconductors possess quasi-free electrons which can be excited to intraband transitions. In non-magnetic materials, the Drude-Lorentz model can be used to model the optical and magneto-optical properties. Analysis shows that if the free carriers are not too heavily damped and the spectral overlap with interband transitions is not too strong, the free carriers give rise to a so-called plasma edge where the reflectivity falls from a very large value for $\epsilon_1=0$ to a very low value for $\epsilon_1=1$, where ϵ_1 is the dielectric constant. In an applied magnetic field the dielectric function is modified by the cyclotron frequency (ω_c), and the reflectivity minimum near the plasma energy for right and left circularly polarized light is shifted by $\pm \hbar\omega_c/2$, where $\hbar$ is Plank's constant divided by 2π . In magnetic materials, the spin-orbit energy is substituted for the cyclotron energy. In general, there are very few ferromagnetic metals with a clear separation in energy of the interband and intraband transitions. Also, an ordering temperature above room temperature requires a strong interaction among the magnetic electrons which tends to oppose a small damping of the free carriers [6].

1.3.4. Some Important Experimental Findings

The largest magneto-optical Kerr rotation was recently discovered in CeSb. The Kerr angle reached a maximum of 90° at 1.5K in an applied field of 5T. This rotation is over 6 times greater than the previous record rotation of 14° found in the same material at higher energies. It is also nine times greater than the next highest rotation of 10° found in EuSe. A 90° rotation is actually the highest possible observable rotation. A further increase above 90° would appear equivalent to a negative rotation with magnitude lower than 90° [7].

Several manganese compounds have shown promise for use in magneto-optical applications; however most have some drawback associated with them. A summary of Kerr rotation data for several manganese compounds is given in Table 1.1.

The main problem associated with MnBi is that it undergoes a first order phase transformation and is not thermally stable. Most work has focused on finding additions that act as stabilizers. PtMnSb lacks sufficiently high perpendicular anisotropy for magneto-optical storage. As a comparison, first generation commercial magneto-optical discs use a material with a Kerr rotation between 0.2 and 0.3 degrees [6].

Table 1.1. Room temperature Kerr rotations for several manganese compounds.

Compound	T_C (K)	$ \theta_K $ (deg)	$h\omega$ (eV)	Reference
MnBi	655	1.2	1.8	[8]
MnBiAl	~650	3.2	1.9	[9]
$R_{0.12}\text{MnBi}$	633	2.54	1.9	[10]
MnSb	555	0.3	2.3	[11]
PtMnSb	585	2.0	1.7	[6]
MnAs	305	0.14	1.5	[11]

1.4. Previous Work on RMn_6Sn_6

The magnetic properties of the RMn_6Sn_6 series have been studied on polycrystalline samples. However, these measurements do not allow one to more carefully study the spin reorientation processes and meta-magnetic (field-induced) transitions that occur in many of the compounds of the series. Also, no measurements have been made of the magneto-optical properties of these compounds.

The compound RMn_6Sn_6 has been shown to form for $R=\text{Y}$, Sc , and Nd-Lu (except for $R = \text{Pm}$, Eu , and Yb which have never been prepared). Attempts at preparing LaMn_6Sn_6 and CeMn_6Sn_6 have failed [12][13]. For the light rare-earth elements (Nd , Pr , and Sm) the crystal structure is orthorhombic (structure type HoFe_6Sn_6 ; Space Group [S.G.] Immm)[12], while the crystal structure for the heavy rare earth elements is hexagonal (structure type HfFe_6Ge_6 ; S.G. P6/mmm)[14]. The atom positions and site symmetries for the HfFe_6Ge_6 crystal structure are given in Table 1.2. The heavy rare

Table 1.2. Atom positions and site symmetries for the HfFe_6Ge_6 crystal structure.

Atom	Position	Symmetry	x	y	z
R	1(b)	6/mmm	0	0	1/2
Mn	6(i)	mm	1/2	0	0.251
Sn1	2(e)	6mm	0	0	0.162
Sn2	2(d)	$\bar{6}m2$	1/3	2/3	1/2
Sn3	2(c)	$\bar{6}m2$	1/3	2/3	0

earth compounds are also more thermodynamically stable: the light rare earth compounds have only been found to form during low temperature annealing ($\sim 545^\circ\text{C}$) for long periods of time[12]. For this reason only the heavy rare-earth compounds have been investigated in this study.

The compound RMn_6Sn_6 orders ferrimagnetically between 435K and 376K for $\text{R}=\text{Gd-Ho}$. All of these except GdMn_6Sn_6 have also been shown to undergo a change in the easy axis of magnetization; however, these transition have not been well characterized. ErMn_6Sn_6 shows a more complex magnetic behavior. It has been proposed that the compound orders antiferromagnetically in low magnetic fields (less than 3kOe) and ferrimagnetically in high fields. The magnetization versus field curves exhibit metamagnetic transitions with critical fields which increase with temperature. There is also a low temperature transition which has been attributed to an ordering of the Er sublattice. The magnetic properties of TmMn_6Sn_6 also exhibit two transitions which correspond to the antiferromagnetic ordering of the Mn and Tm sublattices. The compounds formed with the non-magnetic rare earth elements (Y, Lu, and Sc) order antiferromagnetically between 333K and 384K respectively [15].

A large coercivity of 11 kOe has been found in TbMn_6Sn_6 at 4.2 K by Venturini et al. [15]. Later work by Hu et al. showed that the coercivity was low at 77K and increased to 13 kOe at 200K where it then began to decrease [16]. These results seem contradictory and may be related to the fact that the samples used by the second set of authors were not completely single phase.

Neutron diffraction experiments have also been carried out on RMn_6Sn_6 for $\text{R}=\text{Tb, Ho, Lu, Y, and Sc}$. For Tb and Ho the lanthanide and manganese atoms are

distributed in alternate layers stacked along the c-axis with the sequence Mn-R-Mn-Mn-R-Mn. In the temperature range studied (2-300 K), both exhibited a collinear ferrimagnetic arrangement achieved through the stacking of ferromagnetic (001) layers of rare earth and manganese with the coupling sequence Mn(+)R(-)Mn(+)Mn(+)R(-)Mn(+). For HoMn_6Sn_6 the magnetic moments lie in the (001) plane while in TbMn_6Sn_6 they deviate by 15° from the c-axis at room temperature. At lower temperatures, both undergo spin reorientation processes, and at 2 K the magnetic moments are 50° from the c-axis for HoMn_6Sn_6 and along the [001] direction for TbMn_6Sn_6 [17]. Both the lanthanide and manganese sublattices order simultaneously probably due to a strong ferromagnetic Mn-Mn intrasublattice exchange and a strong antiferromagnetic Mn-R coupling which also creates a collinear arrangement. It was also found that the magnitude of the magnetic moments for manganese are essentially constant between 2-300 K with only a slight decrease of 10-15% as the temperature decreases. The magnitudes of the magnetic moment for terbium and holmium are highly temperature dependent with the holmium showing an almost linear decrease from 0K to the ordering temperature and the terbium showing a positive deviation from this linear relationship [17].

The magnetic structure of YMn_6Sn_6 , LuMn_6Sn_6 , and ScMn_6Sn_6 are significantly different from TbMn_6Sn_6 and HoMn_6Sn_6 . The former three compounds order antiferromagnetically and the magnetic structure is a flat spiral consisting of ferromagnetic (001) "Mn-Sn-Sn-Mn" sheets stacked along the c axis in the sequence Mn-R-Mn-Sn-Sn-Mn-R-Mn. The magnetic moments change their orientation by about 40° - 60° within the basal plane on going from one R sheet to another. For the series as a whole, the Mn-Mn coupling through the "Mn-Sn-Sn-Mn" slab is found to be ferromagnetic while the coupling through the "Mn-R-Mn" depends on the rare-earth element and yields either ferrimagnetic, antiferromagnetic, or incommensurate arrangements [18,19].

2. EXPERIMENTAL METHODS

2.1. Sample Preparation

Most attempts in the literature to prepare RMn_6Sn_6 samples by arc melting or solid state reaction resulted in multiple phase materials [15]. Preliminary attempts to prepare RMn_6Sn_6 by sealing the metals in a tantalum crucible under a helium atmosphere and heating them in an induction furnace resulted in multiple phase materials. No heat treatment was found that would produce a single phase sample. One of the papers in the literature indicated that RMn_6Sn_6 samples had been prepared by chemical transport in molten tin [15]. Based on this information, a sample was prepared by the flux growth method with the assistance of Dr. Paul Canfield. Flux growth is a route to preparing single crystals in which a material is dissolved in a metallic flux and then slowly cooled so that single crystals precipitate out of the molten flux [20]. Samples of RMn_6Sn_6 for $\text{R} = \text{Gd, Tb, Dy, Ho, Er, Tm, and Lu}$ were prepared using a 4.5 percent dilution in tin, i.e. $(\text{RMn}_6)_{4.5}\text{Sn}_{95.5}$. The weighed amounts of the three elements were packed into an alumina crucible with the tin located on the top of the other elements so that it would cover the other elements when it melted and begin to dissolve them. A "catch crucible" was filled with quartz wool and inverted over the top of the packed crucible. This assembly was sealed in a quartz tube under an argon atmosphere with more quartz wool to pad the crucibles. The sample was heated to 1190°C and slowly cooled to the spin temperature over several days (see Table 2.1 for specific information). While hot, the sample was inverted and spun in a centrifuge, forcing the excess tin into the quartz wool located in

Table 2.1. Sample preparation parameters.

Sample	Spin temperature ($^\circ\text{C}$)	Growth time (hours)
GdMn_6Sn_6	600	32
TbMn_6Sn_6	575	200
DyMn_6Sn_6	600	32
HoMn_6Sn_6	600	32
ErMn_6Sn_6	575	200
TmMn_6Sn_6	575	200
LuMn_6Sn_6	650	60

the catch crucible. This method produced hexagonal single crystals of various sizes (50-200mg). Often the crystals were stuck together in a three dimensional structure.

2.2. X-ray Diffraction

X-ray diffraction was used to confirm that the correct phase had been grown out of the flux and to determine the lattice parameters of the materials. Diffraction analysis was performed with a SCINTAG PAD V two-theta diffractometer. The diffractometer was controlled by a computer and utilized Cu-K α radiation with a graphite monochromator attached to the detector. Samples for the diffractometer were prepared by grinding several crystals into a powder using a mortar and pestle. This powder was then sprinkled on a greased microscope slide which was attached to the diffractometer's sample holder. Each scan was made over the two-theta angular range of 10 to 90 degrees. The diffraction peaks were indexed by comparing them to a theoretical diffraction pattern produced by Crystal Structure Determination, Version 4.11. The two-theta values of the observed peaks were then used to calculate the lattice parameters using a least squares routine.

2.3. Magnetic Measurements

The magnetic measurements have been performed on one of three instruments. The first instrument is a Lakeshore Model 7225 AC susceptometer/DC magnetometer. It has the following features:

- 1) It can operate at temperatures from 2 - 325 K.
- 2) A superconducting magnet capable of producing a maximum field of 5.5T is located in a 60 liter superinsulated liquid helium dewar.
- 3) The 0.25 inch stainless steel sample rod attaches to a stepping motor on top of the cryostat. The bottom end is threaded and attached to a nylon rod which can be screwed onto a nylon sample holder. Samples are attached to the sample holder with varnish.

- 4) A personal computer running ACS7000 and DCM7000 control software controls the temperature controls, pick-up coils, stepping motor, and superconducting magnet [21]

The second instrument is an Oxford Instruments MagLab 2000. It has the following features:

- 1) Two inserts are used for different temperature ranges. The first can be used from 2-400K and the second can be used from 300-900K.
- 2) A superconducting magnet capable of producing a maximum field of 9T is located in a liquid helium dewar which is shielded by a liquid nitrogen jacket.
- 3) There are two sample rods used for the different temperature ranges. The nylon sample rod is for use from 2-400 K and has PEEK sample holders on which samples can be glued with varnish. A stainless steel sample rod with a ceramic sample holder is used with the high temperature insert. The sample rod is positioned by the motor drive unit.
- 4) A personal computer running Object Bench version 3.7 is used to control the temperature controls, pickup coils, motor drive unit, superconducting magnet, and AC current source [22].

The third instrument is a Quantum Design model MPMS 5S. It has the following features:

- 1) It can operate from 2-400K.
- 2) A superconducting magnet capable of producing a maximum field of 5T is located in a liquid helium dewar which is shielded by a liquid nitrogen jacket.
- 3) A stainless steel sample rod is connected to a stepper motor on the top of the cryostat. The bottom of the sample rod was connected to the same PEEK sample holders used with the Oxford instrument.
- 4) A personal computer running Quantum Design software is used to control the temperature control, stepper motor, superconducting magnet, and SQUID sensor.

Two types of magnetic measurements were made during this study: AC susceptibility and DC magnetization. The basic principles behind these measurements is the same on all three of the instruments listed above except that the Quantum Design

instrument uses a SQUID to detect the flux rather than the pickup coils found in the other two instruments.

For AC susceptibility measurements, a primary coil is excited by driving an AC current through it. Located inside the primary coil are two secondary coils which have been carefully balanced so that when there is no sample present in either coil, the coils produce identical signals. Thus, when the two signals are subtracted the result is zero. If a magnetic sample is introduced into one of the coils, the impedance of that coil is affected, and the voltage induced will differ from the no sample case. Now when the signals from the two coils are subtracted the resultant is no longer zero. The in and out of phase portions of the resultant are related to the real and imaginary parts of the AC susceptibility respectively by the following equations:

$$\chi' = \alpha X / mfH_{rms}.$$

$$\chi'' = \alpha Y / mfH_{rms}.$$

where α is a calibration coefficient, m is the mass of the sample, and the applied AC signal has an root-mean-square magnitude of H_{rms} and a frequency of f . X and Y are the in and out of phase components of the voltage respectively.

For DC magnetization measurements, a sample is moved through a pair of pickup coils which induces a voltage proportional to the moment. This can be written as:

$$m = - \alpha \int v \, dt,$$

where m is the moment, α is a calibration factor, v is the voltage which is integrated with respect to time. The mass magnetization can then be found by dividing the moment by the mass of the sample [21].

2.4. Magneto-optical Measurements

The polar magneto-optical Kerr effect was measured by Rudiger Lange (Condensed Matter Physics) using a home-built system. All of the samples were measured at room temperature with a magnetic field applied by a Nd-Fe-B permanent magnet (approximately 0.3-0.4T depending on the sample mounting). $TbMn_6Sn_6$ was also measured at low temperatures inside of an optical cryostat with a magnetic field

applied by a 7 Tesla split coil superconducting magnet. GdMn_6Sn_6 , TbMn_6Sn_6 , and DyMn_6Sn_6 were measured in the as-grown condition. HoMn_6Sn_6 , ErMn_6Sn_6 , TmMn_6Sn_6 , and LuMn_6Sn_6 were lightly polished to remove excess flux to obtain a smooth surface for the measurement. TbMn_6Sn_6 was measured in both the as-grown and polished condition to determine the effect the polishing had on the results. The samples were polished with 600 grit SiC paper, 1200 grit SiC paper, and finally with Linde A alumina polishing media.

Figure 2.1 schematically shows the setup used for the measurements. The light source is a Xe short-arc lamp. Mirror 1 (M1) is used to focus the light on the sample via a folding mirror (M2). The light is linearly polarized by P with its transmission axis along the vertical. The light is then reflected off of the sample which is either mounted in the cryostat or on a Nd-Fe-B magnet. Mirror 3 (M3) is a plane mirror used to fold the beam and mirror 4 (M4) focuses the reflected beam onto the entrance slit of a $\frac{1}{4}$ -m-monochromator. The beam passes a photoelastic modulator (M) with its fast axis at zero before going through an analyzer (A) at 45° . The shutter (S) is used to measure dark signals and a filter (F) removes higher order light at the photo detector (PM). The

Figure 2.1. MOKE experimental setup.

polarizer and analyzer prisms are mounted in rotary stages and can be controlled by a computer.

There are two methods for measuring the Kerr effect: the intensity method and the compensation method. The first technique uses the photoelastic modulator and no other moving element. The Kerr rotation is found using the ratio of the DC and 2f signals and the ellipticity is found from the ratio of the DC and 1f signals. Where the 1f and 2f signals are the first and second harmonic respectively. The following equations are used:

$$\theta_K = -\frac{B}{4J_2(\delta_0)} \frac{I_{2f}}{I_{DC}}$$

$$\varepsilon_K = -\frac{A}{4J_1(\delta_0)} \frac{I_{1f}}{I_{DC}}$$

where $J_i(\delta_0)$ are Bessel functions of order i , and δ_0 is the amplitude of the modulation. A and B are calibration coefficients. The intensity method is easy, fast, and highly accurate as long as the rotation is small and the light intensity is sufficiently bright. This method is used for room temperature measurements when the cryostat is not used. It should be noted that when the cryostat is used there is a large Faraday rotation in the optical windows which can produce a background rotation of 60° at 6T (5eV) and requires the use of the second method.

The compensation method is used when large Kerr rotations are present. The detected 2f signal is given by:

$$I_{2f} = \frac{1}{2} J_2(\delta_0) \cos(2\varepsilon_K) \sin(2(\varphi + \theta_K)),$$

where φ is the angle the polarizer has been rotated from the vertical. Therefore, the Kerr rotation can be found by simply rotating the polarizer until the 2f signal vanishes. Inserting a quarter wave plate (C) allows one to measure the ellipticity by eliminating the 2f signal. The accuracy of this method does not depend on the background since the entire rotation is always being compensated for. The background can be determined by measuring the rotation of the reflection off of an aluminum mirror since aluminum has been found to have a Kerr rotation of essentially zero.

2.5. Corrosion Properties

In order to test the corrosion resistance of the samples, a relatively simple test was used. A sample was weighed to 4 decimal places. It was then placed in the open atmosphere which was relatively stable at $\sim 22^{\circ}\text{C}$. The sample was re-weighed at regular intervals over a 3 month time period.

3. DATA ANALYSIS

3.1. Crystal Structure

The crystal structure of all of the RMn_6Sn_6 compounds had been determined previously in the literature. The x-ray diffraction results confirmed that the crystal structure is type HfFe_6Ge_6 (space group $P6/\text{mmm}$) for all the compounds tested. The lattice parameters are shown in Table 3.1 and the unit cell volume is plotted as a function of the lanthanide element in Figure 3.1. A small amount of elemental tin was seen in the diffraction patterns of some of the samples. It probably originates from small amounts of

Table 3.1. Lattice parameters.

Sample	a (Å)	c (Å)
GdMn_6Sn_6	5.5387	9.0291
TbMn_6Sn_6	5.5302	9.0208
DyMn_6Sn_6	5.5260	9.0113
HoMn_6Sn_6	5.5214	9.0060
ErMn_6Sn_6	5.5177	9.0006
TmMn_6Sn_6	5.5136	8.9955
LuMn_6Sn_6	5.5073	8.9907

Figure 3.1. Unit cell volume as a function of lanthanide element.

flux that remained on the surface of the crystals after they were spun.

The lanthanide contraction is clearly seen in Figure 3.1. The plot of the unit cell volume is almost linear with the exception of the end members gadolinium and lutetium which both deviate above this line. This anomaly was verified using two additional diffraction scans. This seems to correspond with the positive deviation of the metallic radii of gadolinium and lutetium with respect to the linear variation seen in the metallic radii of the other heavy lanthanide elements. Both sets of deviations probably arise from crystal-field effects. It is thought that the lanthanides which do not have spherical 4f wave functions undergo a crystal-field contraction. This contraction would not be present in lutetium because its 4f shell is completely full or in gadolinium because its half-filled shell is spherically symmetrical [1].

3.2. Magnetic Properties

The magnetic properties of TbMn_6Sn_6 , HoMn_6Sn_6 , ErMn_6Sn_6 , TmMn_6Sn_6 , and LuMn_6Sn_6 were measured in three crystallographic directions: a, b, and c. The b direction has been defined to be the direction perpendicular to both a and c and lies parallel to the basal plane of hexagonal unit cell. Measurements with the magnetic field parallel to the b axis ($H||b$) yielded results almost identical to those taken with the magnetic field parallel to the a axis ($H||a$) for all the samples measured. This indicates that the moments do not have a preferable direction in the basal plane. It has also been found for all the compounds studied that there is no frequency dependence; therefore, these results will not be discussed further.

3.2.1. GdMn_6Sn_6

The DC magnetization curve at 300K for GdMn_6Sn_6 with $H||c$ is shown in Figure 3.2. The magnetization curve was measured so that the magnetization values could be correlated with the magneto-optics results.

Figure 3.2. DC magnetization curve at 300K for GdMn₆Sn₆ with H||c.

3.2.2. TbMn₆Sn₆

The AC field dependence of the AC susceptibility for TbMn₆Sn₆ with H||c is shown in Figure 3.3. Increasing the AC field tends to shift the beginning of the main feature to lower temperatures, while the high temperature end is unaffected. The AC susceptibility was measured under various DC field biases, and the results are shown in Figure 3.4. An applied DC field decreases the size of the main transition. The DC magnetization curves are shown in Figure 3.5 and 3.6. The magnetization curves show hysteresis at low temperatures (5-80K). At intermediate temperatures (up to 300K), the curves reach saturation very quickly. Above this temperature there is evidence of field induced transitions with critical fields that increase with increasing temperature. The AC field dependence of the AC susceptibility for TbMn₆Sn₆ with H||a is shown in Figure 3.7. An increased AC field decreases the size of the plateau-like feature. The DC field dependence of the AC susceptibility is shown in Figure 3.8. An applied DC field removes the large plateau feature and lowers the transition temperature as the applied DC field

Figure 3.3. AC field dependence of the AC susceptibility for $TbMn_6Sn_6$ with $H||c$.

Figure 3.4. DC field dependence of the AC susceptibility for $TbMn_6Sn_6$ with $H||c$.

Figure 3.5. DC magnetization curves for TbMn₆Sn₆ with H||c at low temperatures.

Figure 3.6. DC magnetization curves for TbMn₆Sn₆ with H||c at high temperatures.

Figure 3.7. AC field dependence of the AC susceptibility for $TbMn_6Sn_6$ with $H||a$.

Figure 3.8. DC field dependence of the AC susceptibility for $TbMn_6Sn_6$ with $H||a$. The inset shows a portion of the main figure in more detail and has the same units on the axes.

is increased. The DC magnetization curves are shown in Figure 3.9 and Figure 3.10. The low temperature magnetization curves show meta-magnetic transitions with critical fields that decrease with increasing temperature. The high temperature curves saturate quickly. The temperature dependence of the critical fields has been combined with the DC field dependence of the AC susceptibility transitions in Figure 3.11. The two sets of data match up closely. The figure also includes the transitions seen with $H||c$. By comparing the AC susceptibility measured in the two directions, the c direction seems to be the easy axis up to 310K, and the a and b directions seem to be the easy axis (easy plane) above that temperature. Also, it is reasonable that below this temperature, as a field is applied parallel to the a direction the moments will be pulled into the a direction when a sufficiently large field is applied. This is seen in the magnetization curves which exhibit field induced transitions. At lower temperatures, a larger field is required to flip the moments. With a field applied parallel to the c direction, the moments can be flipped into the c direction above 310K. Thus, a field applied parallel to the a direction shrinks the

Figure 3.9. DC magnetization curves for TbMn_6Sn_6 with $H||a$ at low temperatures.

Figure 3.10. DC magnetization curves for TbMn₆Sn₆ with H||a at high temperatures.

Figure 3.11. Transition temperatures as a function of DC field for TbMn₆Sn₆. The easy axis has been labeled for the high temperature and low temperature regions.

size of the temperature range where the moments are in the c direction, and a field applied parallel to the c direction increases the size of the same region. The temperature of the spin-reorientation transition is slightly lower than 330K which was reported in the literature [15].

The high temperature transition occurs at about 450K for both orientations and probably corresponds to a ferrimagnetic to paramagnetic transition. This value is slightly higher than 423K, which was previously reported in the literature [15]. The saturation magnetization from the 4.5K magnetization curve was used to determine the net moment per formula unit using the lattice parameters and molecular weights. The net moment is $4.04\mu_B$ per formula unit. If one assumes a collinear ferrimagnetic arrangement as was previously determined by neutron diffraction [22], and if one assumes a free ion value for the terbium moment, a moment on the manganese of $2.17\mu_B$ is found. This compares well with the value $2.39\mu_B$ which was found using neutron diffraction [22]; however, it should be noted that the value of the terbium moment reported was $8.57\mu_B$ as opposed to the free ion value of $9.0\mu_B$. Comparisons with other compounds in the series will provide some insight into this discrepancy.

The inverse DC susceptibility at 5T has been plotted as a function of temperature in Figure 3.12 for both $H||a$ and $H||c$. The closed symbols indicate data points that were included in the least squares regression analysis, while the open symbols indicated data points that seemed to depart from the linear relationship. A linear least squares regression was used to determine an effective moment per formula unit of $5.64\mu_B$ with $H||c$ and $4.39\mu_B$ with $H||a$. This is significantly smaller than the value of $12.24\mu_B$ found in the literature [15]. It is also smaller than the free ion value of terbium ($7.94\mu_B$) which does seem logical. One possible explanation is the fact that previous authors found the inverse susceptibility strongly deviated from the linear relationship below 600K and that region of the curve had a much higher slope, similar to that found in this study [15]. Unfortunately, in the temperature range where the linear relationship exists, the moment is smaller than can be measured precisely with the apparatus used. This leads to noise at higher temperatures as is seen in Figure 3.12.

Figure 3.12. Inverse susceptibility versus temperature for TbMn₆Sn₆. The straight lines are the results of linear least squares regression.

The paramagnetic Curie temperature was found to be 421K with H||c and 439K with H||a. These values are slightly lower than the ordering temperatures found earlier, but significantly larger than the value of 125K which was found by Venturini et al. [15].

3.2.3. DyMn₆Sn₆

The DC magnetization curve at 300K for DyMn₆Sn₆ with H||c is shown in Figure 3.13. The magnetization curve was measured so that the magnetization values could be correlated with the magneto-optics results.

3.2.4. HoMn₆Sn₆

The AC field dependence of the AC susceptibility of HoMn₆Sn₆ with H||c is shown in Figure 3.14. There is only a small variation with AC field and this occurs only at low temperatures. The AC susceptibility was measured under various DC field biases and the results are shown in Figure 3.15. An applied DC field reduces the size of the broad transition between 50 and 150K, which reveals a second transition that occurs at

Figure 3.13. DC magnetization curve at 300K for DyMn₆Sn₆ with H||c.

Figure 3.14. AC field dependence of the AC susceptibility for HoMn₆Sn₆ with H||c.

Figure 3.15. DC field dependence of the AC susceptibility for HoMn_6Sn_6 with $H||c$.

200K. An applied field also shifts the high temperature transition to slightly lower temperatures. The DC magnetization curves between 10 and 420K are shown in Figure 3.16. The curve at 10K shows some hysteresis, which is not present at higher temperatures. At higher temperatures, the curves become gradually less steep and the sample saturates much more slowly.

The AC field dependence of the AC susceptibility for HoMn_6Sn_6 with $H||a$ is shown in Figure 3.17. There is only a small effect from changing AC fields, and it is limited to the low temperature region. The DC field dependence of the AC susceptibility is shown in Figure 3.18. An applied DC field decreases the size of the plateau feature between 200 and 400K which gives way to two smaller transitions at 180K and 400K. The DC magnetization curves are shown in Figure 3.19. The curves are all very similar up to 340K where a small amount of hysteresis is seen in the first quadrant. At higher temperatures the slope begins to dramatically decrease and the sample saturates much slower. The results shown above seem consistent with earlier work which has shown that there is a spin reorientation process that occurs [17]. This is most easily seen by the fact that the AC susceptibility measured along the c axis falls

Figure 3.16. DC magnetization curves for HoMn₆Sn₆ with H||c.

Figure 3.17. AC field dependence of the AC susceptibility for HoMn₆Sn₆ with H||a.

Figure 3.18. DC field dependence of the AC susceptibility HoMn_6Sn_6 with $H \parallel a$.

Figure 3.19. DC magnetization curves for HoMn_6Sn_6 with $H \parallel a$.

off rapidly between 150 and 225K (Figure 3.12), and the AC susceptibility measured along the a axis continues to increase in this temperature range, reaching a plateau at ~200K (See Figure 3.15). This would seem to indicate that the easy axis is closer to the c axis at low temperatures and rotates to the basal plane between 150 and 200K. Neutron diffraction studies showed that the transition occurred gradually between 125K and 200K [17]. The smaller amount of hysteresis as compared to TbMn_6Sn_6 is also consistent with the fact that the moments in HoMn_6Sn_6 were found to be canted 50° from the c-axis at low temperatures, while they were parallel to the c axis in TbMn_6Sn_6 at low temperatures.

The high temperature peak is most likely a ferrimagnetic to paramagnetic transition and occurs at about 400K in both orientations. This is slightly higher than the ordering temperature of 376K which was reported by Venturini et al. [15]. The value of the moment on the manganese and holmium atoms has been estimated using the magnetization curves at 10K. The net moment per formula unit is $3.26\mu_B$, and if one assumes the free ion value for the holmium atoms and a ferrimagnetic structure, the manganese atoms carry a moment of $2.21\mu_B$. This is in excellent agreement with the value found for the manganese atoms in TbMn_6Sn_6 and is in good agreement with the value found using neutron diffraction, $2.39\mu_B$. However, as was the case for TbMn_6Sn_6 , the value of the moment on the rare earth element determined by neutron diffraction ($8.43\mu_B$) was less than the free ion value ($10\mu_B$) [17].

The inverse DC susceptibility at 5T has been plotted as a function of temperature in Figure 3.20 for both $H||a$ and $H||c$. A linear least squares regression has been used to determine the effective moment and the paramagnetic Curie temperature, θ_p . The effective moment per formula unit is $8.26\mu_B$ with $H||c$ and $8.31\mu_B$ with $H||a$. This is smaller than the value reported in the literature ($13.85\mu_B$), it is also smaller than the free ion value of holmium $10.6\mu_B$ [15]. The same reasons that were used to explain the discrepancy for TbMn_6Sn_6 probably also apply to this sample.

The paramagnetic Curie temperature is 387K with $H||c$ and 382K with $H||a$. This is slightly lower than the ordering temperatures discussed above. It is also much larger than the paramagnetic Curie temperature of 157K reported in the literature [15].

Figure 3.20. Inverse susceptibility versus temperature for HoMn₆Sn₆. The straight lines are the results of linear least squares regression.

3.2.5. ErMn₆Sn₆

The AC field dependence of the AC susceptibility is shown in Figure 3.21 for ErMn₆Sn₆ with H||c. The only effect of increasing the AC field is an increase in the size of the low temperature peak which can be seen clearly in the inset of Figure 3.21. The AC susceptibility was measured under various DC magnetic field biases and the results are shown in Figure 3.22. Increasing applied DC fields flattened the low temperature transition until it vanished at 1 T. An applied DC field also shifted the high temperature peak to lower temperatures. Magnetization curves were measured at various temperatures and can be seen in Figure 3.23, Figure 3.24, and Figure 3.25. The DC magnetization data show meta-magnetic (field-induced) transitions at low temperatures with critical fields that increase with temperature. These transitions have been combined with the transitions seen as a function of DC field on the AC susceptibility plots and the critical fields as a function of temperature seen in the high temperature DC magnetization data. These transitions are plotted in Figure 3.26. It can be seen that the high temperature peak in the AC susceptibility (Figure 3.20) corresponds with the kink seen in the high temperature

AC Field Dependence of X_{ac} vs. Temperature
 ErMn_6Sn_6 - H||c; 1000Hz, $H_{dc} = 0\text{T}$

Figure 3.21. AC field dependence of the AC susceptibility of ErMn_6Sn_6 with H||c. The inset shows the low temperature transition in more detail and the axes have the same units.

DC Field Dependence of X_{ac} vs. Temperature
 ErMn_6Sn_6 - H||c; $H_{ac} = 10\text{Oe}$, 1000Hz

Figure 3.22. DC field dependence of the AC susceptibility of ErMn_6Sn_6 with H||c. The inset shows the low temperature transition in greater detail and both the axes have the same units.

Figure 3.23. DC magnetization curve at low temperatures for ErMn₆Sn₆ with H||c.

Figure 3.24. DC magnetization curve at intermediate temperatures for ErMn₆Sn₆ with H||c.

Figure 3.25. DC magnetization curve at high temperatures for ErMn₆Sn₆ with H||c.

Figure 3.26. Transition temperatures versus applied DC field for ErMn₆Sn₆ with H||c. The magnetic structure of the various regions have been labeled.

DC magnetization data (Figure 3.25). Critical fields could not be found at intermediate temperatures (150-250K) because the transitions were not well defined.

The AC field dependence of the AC susceptibility for ErMn_6Sn_6 with $H||a$ can be seen in Figure 3.27. Increasing the size of the AC field increases the size of the low temperature peak as was the case with $H||c$. It should be noted that the relative size of the low temperature and high temperature transitions have been reversed as one goes from $H||c$ to $H||a$; however, the temperature of the transitions remains constant. This may indicate that the moments in the low temperature transition have an easy axis parallel to the basal plane, and the moments associated with the high temperature transition prefer the c direction. The DC field dependence of the AC susceptibility for ErMn_6Sn_6 with $H||a$ is shown in Figure 3.28 and 3.29. As the DC bias is increased, the low temperature transition moves to higher temperatures, and the high temperature transition is shifted to lower temperatures. Most of the curves still show a broad hump near 350 K, the transition temperature seen with zero DC bias. When one reaches a DC field of 1.75T, the two transitions have reached a common temperature of 225 K. Above 1.75T, this transition is

Figure 3.27. AC field dependence of the AC susceptibility for ErMn_6Sn_6 with $H||a$.

Figure 3.28. DC field dependence of the AC susceptibility for ErMn_6Sn_6 with $H \parallel a$ for low applied DC fields.

Figure 3.29. DC field dependence of the AC susceptibility for ErMn_6Sn_6 with $H \parallel a$ for high applied DC fields. The zero field curve has been removed so that the other transitions can be seen more clearly.

suppressed, and at 3T only the broad transition at 350K is seen.

The DC magnetization curves for ErMn_6Sn_6 with $H||a$ are seen in Figure 3.30 and Figure 3.31. A meta-magnetic transition is seen in almost all the curves. The critical field first increases with increasing temperature up to 220K, and then decreases with increasing temperature. Temperature dependence of these critical fields has been combined with the DC field dependence of the transitions seen in the AC susceptibility data and is shown in figure 3.32. The two sets of data agree very well and outline the same field-temperature curves. It is significant that the critical fields are much lower with $H||a$ (Figure 3.32) than with $H||c$ (Figure 3.26); however, there does appear to be some similarity in the shape of the two sets of curves.

In order to understand the structure, the effective moment per formula unit was calculated at 5K. This yielded a moment of $4.20\mu_B$, and if one assumes the free ion value for the erbium atoms, a ferrimagnetic structure yields a moment on the manganese atoms of $2.20\mu_B$. This is in excellent agreement with the values determined for the manganese atoms in the case of the TbMn_6Sn_6 and HoMn_6Sn_6 . This is a strong indication that the

Figure 3.30. DC magnetization curve at low temperatures for ErMn_6Sn_6 with $H||a$.

Figure 3.31. DC magnetization curve at high temperatures for ErMn₆Sn₆ with H||a.

Figure 3.32. Transition temperatures versus applied DC field for ErMn₆Sn₆ with H||a. The magnetic structure of the various regions have been labeled.

high field region in Figure 3.32 is ferrimagnetic. It then seems likely that the field induced transitions are antiferromagnetic to ferrimagnetic transitions. There are two temperature transitions that must be accounted for in the zero DC field AC susceptibility. As was previously suggested by Venturini et al., these probably correspond to the antiferromagnetic ordering of the erbium and manganese sublattices [17]. The transition temperatures at zero field were found to be 65K and 350K in this study (see Figure 3.26 or 3.32) which are close to 75K and 352K respectively, which are the values reported by Venturini et al. [15]. By comparing the DC field dependence of the low temperature peak for the two different orientations, there is an indication that it is much easier to flip the moments from the antiferromagnetic structure to the ferrimagnetic structure when the magnetic field is applied in the a direction. This is also seen by the fact that the transitions occur at lower fields for all temperatures with $H||a$. Because the moments are flipped so easily below 50K with $H||a$, it is hard to determine the exact size of the region in which both the manganese and erbium sublattices are antiferromagnetic from the given data. The controlling interactions in this case appears to be the Mn-Mn interaction which controls whether the manganese sublattice is antiferromagnetic or ferromagnetic, and the Er-Mn interaction which forces the erbium sublattice to order ferromagnetically and antiparallel to the manganese sublattice whenever the manganese is ferromagnetic.

The inverse DC susceptibility at 5T has been plotted as a function of temperature in Figure 3.33 for $H||c$. The results from a linear least squares regression indicate a moment per formula unit of $6.37\mu_B$ for $H||c$. The data for $H||a$ has too much noise to give a good linear fit. This is smaller than the value in the literature ($12.91\mu_B$) [15], and is also smaller than the free ion value of erbium ($9.6\mu_B$). This can be accounted for by the changing slope seen in the inverse susceptibility data presented in the literature [15].

The paramagnetic Curie temperature with $H||c$ is 417K which is slightly larger than the ordering temperatures listed above. It is also much larger than 241K, the paramagnetic Curie temperature found in the literature [15].

Figure 3.33. Inverse susceptibility versus temperature for ErMn₆Sn₆. The straight line is the results of linear least squares regression.

3.2.6. TmMn₆Sn₆

The AC field dependence of the AC susceptibility of TmMn₆Sn₆ with H||c is shown in Figure 3.34. As is clear from the figure, there is no AC field dependence. The DC field dependence is shown in Figure 3.35 and it can be seen that the peak in the susceptibility at 350 K is shifted to lower temperatures by an applied DC field. The field dependence of this transition temperature is shown in the inset of Figure 3.35. The DC magnetization curves are shown in Figure 3.36, and they are all linear with the exception of the curves at 300 and 340 K which begin to depart negatively from linearity at high fields. The AC field dependence of the AC susceptibility of TmMn₆Sn₆ with H||a is shown in Figure 3.37. Again, there is no AC field dependence, but a low temperature transition at 40 K is seen where none was evident in the measurements taken with H||c. The DC field dependence of the AC susceptibility shows a very complex behavior as seen in Figure 3.38. At some DC fields, there are as many as 3 transitions. The DC

Figure 3.34. AC field dependence of the AC susceptibility for $TmMn_6Sn_6$ with $H||c$.

Figure 3.35. DC field dependence of the AC susceptibility for $TmMn_6Sn_6$ with $H||c$.

Figure 3.36. DC magnetization curves for TmMn₆Sn₆ with H||c.

Figure 3.37. AC field dependence of the AC susceptibility for TmMn₆Sn₆ with H||a.

Figure 3.38. DC field dependence of the AC susceptibility for $TmMn_6Sn_6$ with $H||a$.

magnetization curves are shown in Figure 3.39 and Figure 3.40. The low temperature and high temperature data have been separated so that the plot is less confusing. Most of the curves show meta-magnetic transitions with critical fields that initially increase with increasing temperature up to 100K. Above this temperature the critical fields begin to decrease with increasing temperature. The critical fields have been defined to be the point at which there is a discontinuity in the slope of the magnetization. These critical fields are shown in Figure 3.41 as a function of temperature with the DC field dependence of the transitions in the AC susceptibility. The DC and AC data show fairly good agreement. Some data points have been added from curves that do not appear in Figures 3.38, 3.39 or 3.40. These curves were omitted to avoid making the figures too jumbled. The transitions seem to map out 6 distinct regions.

As a first step in the analysis, the effective magnetic moment per formula unit was calculated using the magnetization curve for $H||a$ at 5K. The effective moment is $6.30 \mu_B$, and if one assumes the free ion value for the thulium atoms and a ferrimagnetic structure as was found in the other compounds of the series, the manganese atoms must each carry

Figure 3.39. DC magnetization curve at low temperatures for TmMn₆Sn₆ with H||a.

Figure 3.40. DC magnetization curve at high temperatures for TmMn₆Sn₆ with H||a.

Figure 3.41. Transition temperatures versus applied DC field for TmMn₆Sn₆ with H||a. The magnetic structure of the various regions have been labeled.

a moment of $2.22 \mu_B$. This is in excellent agreement with the moments found for the manganese atoms in the previous three compounds, ErMn₆Sn₆, HoMn₆Sn₆, and TbMn₆Sn₆, which is a strong indication that the structure at high fields and low temperatures is ferrimagnetic. This would mean that the field transition at low temperature is antiferromagnetic to ferrimagnetic.

Above 100K, the general shape of the magnetization curves for H||a is much different than the low temperature curves. It appears that the moments are not completely flipped. By looking at the moment associated with the transition at 80K ($8.02 \mu_B$) and comparing it to the moment associated with the transition at 120K ($3.83 \mu_B$), it seems likely that during the field induced transition at 120K, one half of the moments are flipped. For example, with 12 antiferromagnetic moments there would be 6 up moments and 6 down moments. By flipping half of the down moments, one would obtain 9 up and 3 down. This would equal a net of 6 up moments or one-half of the value expected if all 6 down moments were flipped.

The two transitions seen in the AC susceptibility under zero DC bias are most likely the antiferromagnetic ordering of the thulium and manganese sublattices as was seen in ErMn_6Sn_6 and suggested by Venturini et al. [15]. The ordering temperatures found in this study were 40K and 350K-360K as compared to 58K and 347K as determined by Venturini et al. [15]. It should also be noted that the easy axis is in the basal plane. This seems clear since it was not possible to flip the moments with $H\parallel c$ even with an applied field of 9T.

The inverse DC susceptibility at 5T has been plotted as a function of temperature in Figure 3.42 for both $H\parallel a$ and $H\parallel c$. A linear least squares regression has been used to determine the effective moment and the paramagnetic Curie temperature θ_p . The effective moment per formula unit was found to be $8.03\mu_B$ for $H\parallel c$ and $7.52\mu_B$ for $H\parallel a$. These values are smaller than both the value reported in the literature ($11.42\mu_B$) and the free ion value of thulium ($7.6\mu_B$). The paramagnetic Curie temperature is 393K for $H\parallel c$ and 401K for $H\parallel a$. These values are slightly larger than the ordering temperature and much larger than 304K, the value reported by Venturini et al. [15].

Figure 3.42. Inverse susceptibility versus temperature for TmMn_6Sn_6 . The straight lines are the results of linear least squares regression.

3.2.7. LuMn_6Sn_6

The AC field dependence of the AC susceptibility of LuMn_6Sn_6 with $H||c$ is shown in Figure 3.43. As is clear from the figure, there is no AC field dependence. The curves are essentially featureless. The DC field dependence is shown in Figure 3.44 and there seems to be little DC field dependence with the exception of a small transition at 340K which becomes apparent in a field of 3T. The DC magnetization curves are shown in Figure 3.45. The DC magnetization curves are also very simple showing a simple linear relationship which only has a weak temperature dependence.

The AC field dependence of the AC susceptibility of LuMn_6Sn_6 with $H||a$ is shown in Figure 3.46. There is no AC field dependence and there is an indication that a transition occurs at a temperature just over 400K. Unfortunately, attempts to obtain AC susceptibility data above 400K with this sample failed due to the poor sensitivity at high temperatures and the weak signal associated with this sample. This transition is probably

Figure 3.43. AC field dependence of the AC susceptibility for LuMn_6Sn_6 with $H||c$.

Figure 3.44. DC field dependence of the AC susceptibility for LuMn_6Sn_6 with $H \parallel c$.

Figure 3.45. DC magnetization curves for LuMn_6Sn_6 with $H \parallel c$.

Figure 3.46. AC field dependence of the AC susceptibility for LuMn_6Sn_6 with $H \parallel a$.

the antiferromagnetic ordering of the manganese sublattice which was seen at 353K by Venturini et al. [15].

The DC field dependence of the AC susceptibility of LuMn_6Sn_6 with $H \parallel a$ is shown in Figure 3.47. An applied DC field creates a broad transition between 200 and 350K with the beginning of the transition moving to lower temperatures as a higher field is applied. Figure 3.48 shows the low temperature DC magnetization curves for LuMn_6Sn_6 with $H \parallel a$ which exhibit a field induced transition with critical fields that increase up to 120K and then begin to decrease. The high temperature DC magnetization curves are shown in Figure 3.49, and the curves above 200K do not exhibit any field induced transitions. These transitions have been defined by the discontinuity in the slope of the magnetization curve and are mapped out in Figure 3.50 along with the transitions in the AC susceptibility.

The sample has not approached saturation at 9T for either $H \parallel c$ or $H \parallel a$. This makes it difficult to calculate a moment from the magnetization curves. One can only say that the moment associated with each manganese atom is greater than $0.75\mu_B$ (assuming a collinear arrangement). This also makes it difficult to determine the type of transition that

Figure 3.47. DC field dependence of the AC susceptibility for LuMn_6Sn_6 with $H \parallel a$.

Figure 3.48. DC magnetization curves at low temperatures for LuMn_6Sn_6 with $H \parallel a$.

Figure 3.49. DC magnetization curves at high temperatures for LuMn₆Sn₆ with H||a.

Figure 3.50. Transition temperatures as a function of DC field for LuMn₆Sn₆ with H||a. The magnetic structure of the various regions have been labeled.

occurs in the DC magnetization curves, but it probably a partial flipping of the moments from antiferromagnetic to ferromagnetic as was seen in TmMn_6Sn_6 .

The inverse DC susceptibility at 5T has been plotted as a function of temperature in Figure 3.51 for both $H\|a$ and $H\|c$. A linear least squares regression has been used to determine the effective moment and the paramagnetic Curie temperature θ_p . The effective moment per formula unit was found to be $6.48\mu_B$ for $H\|c$ and $5.68\mu_B$ for $H\|a$. These values are smaller than both the value reported in the literature ($8.51\mu_B$) [15]. Since lutetium does not carry any moment, this means that each manganese has a moment of $2.65\mu_B$ for $H\|c$ or $2.32\mu_B$ for $H\|a$ ($\mu_{\text{eff}} = (6\mu_{\text{Mn}}^2)^{1/2}$). These are smaller than the values reported by Venturini et al.; however, they are similar to the values found for the moment on the manganese atoms using the magnetization curves in the other RMn_6Sn_6 compounds studied. Microprobe analysis indicated that the stoichiometry of the sample matched the ideal case (LuMn_6Sn_6) within the standard deviation of the measurement. It should also be noted that it was difficult to fit the inverse susceptibility to a straight line due to its curvature. The paramagnetic Curie temperature is 416K for $H\|c$ and 411K for $H\|a$. These values are slightly larger than the ordering temperature ($\sim 400\text{K}$) and similar to the value of 406K reported by Venturini et al. [15].

Figure 3.51. Inverse susceptibility versus temperature for LuMn_6Sn_6 . The straight lines are the results of linear least squares regression.

3.3 Magneto-optical Properties

The magneto-optical properties were measured on all the samples such that the applied magnetic field and the incident radiation were parallel to the c axis of the sample. Some of the samples had small amounts of flux on the surface, and attempts to grow samples without flux on the surface failed. Therefore, these samples needed to be polished in order to obtain a clean surface; however, it has been found that polishing can affect the Kerr rotation [11]. In order to determine the effect of polishing on the samples, TbMn_6Sn_6 was measured first in the as grown condition (which had a smooth surface) and was then measured again after it had been lightly polished. Measurements were taken at room temperature in an applied field of 0.55T, and the results are shown in Figure 3.52. Polishing did reduce the Kerr rotation as expected; however the effect was relatively minor and it affected the magnitude of the curve while having little effect on the structure seen. This indicates that the polished samples may have a decreased Kerr rotation and this should be considered when analyzing those results.

Figure 3.52. Effect of polishing on the polar Kerr effect at 295K and 0.55T with $H \parallel c$.

The temperature dependence of the Kerr rotation was also studied. The Kerr rotation was measured on TbMn_6Sn_6 at 100K in an applied field of 1.5T and is compared to the room temperature measurement in Figure 3.53. The structure remains approximately the same at both temperatures; however, the magnitude is increased by a factor of about 15%. If one examines the magnetization curves seen earlier in Figure 3.5, it is clear that the increase in the applied magnetic field is not the reason for the increase since the magnetization curves are essentially flat above 0.4T. It can also be seen from the magnetization curve that the magnetization decreases with increasing temperature which would seem to contradict the Kerr rotation results. An explanation can be found if one examines the temperature dependence of the magnetic moments in TbMn_6Sn_6 which were determined by neutron diffraction [17]. Idrissi et al. found that the magnetic moment on the manganese atoms increased by a factor of about 10-15% from 300 K to 100 K (the scale of their figure prevents an exact value from being determined). This

Figure 3.53. Temperature dependence of the polar Kerr effect with $H||c$.

seems to suggest that the value of the Kerr rotation in TbMn_6Sn_6 does not depend on the magnetization, but on the value of the moment on the manganese atoms.

Room temperature magneto-optical spectra of RMn_6Sn_6 for $\text{R}=\text{Gd}$, Tb , Dy , Ho , Er , and Tm are shown in Figure 3.54 and Figure 3.55. The rotation and ellipticity have been placed on separate graphs to make the figures clearer. Measurements were made at 0.3-0.55T (see Table 3.2).

The Kerr rotations for the compounds containing different lanthanide elements appear to have similar structures with a maxima near 1.8eV and a minima near 2.4eV. The ellipticities show a maxima near 2.0eV. The main differences in the curves lies in the magnitude of the rotation. Close examination reveals that there is also a slight shift in the energy associated with the main features. The minima in the rotation occurs at 2.4eV in GdMn_6Sn_6 , TbMn_6Sn_6 , and DyMn_6Sn_6 ; and at 2.5 eV in HoMn_6Sn_6 , ErMn_6Sn_6 , and TmMn_6Sn_6 . A similar trend is seen in the maxima in the ellipticity. The maxima shifts

Figure 3.54. Room temperature polar Kerr rotation with $\text{H}||\text{c}$.

Figure 3.55. Room temperature polar Kerr ellipticity with $H \parallel c$.

Table 3.2. Magneto-optical measurements information summary.

R	$ \theta_K _{\min}$ (deg)	Kerr min (eV)	Ellipticity max (eV)	H_{applied} (T)	M (at H_{applied}) (emu/g)	$M_{\text{saturation}}$ (emu/g) [†]	$M/M_{\text{saturation}}$
Gd	0.104	2.4	1.8	0.4	5.64	24.11	0.234
Tb	0.225	2.4	2.0	0.55	23.40	24.57	0.952
Dy	0.016	2.4	2.1	0.4	9.76	22.90	0.426
Ho	0.070	2.5	2.1	0.4	7.84	28.10	0.279
Er	0.025	2.5	2.2	0.3	2.32	30.91	0.075
Tm	0.004	2.5	2.2	0.4	1.81	36.28	0.050
Lu				0.4	1.12	33.45	

[†]As measured at 300K.

to higher energies as one moves to heavier lanthanide elements. It occurs at 1.8 eV in GdMn_6Sn_6 and shifts to 2.2 eV in TmMn_6Sn_6 (See Table 3.2). The shift in the energy of the ellipticity maxima is shown in Figure 3.56. If one draws a linear least squares regression line through the data points for $R=\text{Tb-Tm}$ and extrapolates it back to gadolinium, one can see that the value for gadolinium deviates from this line in the same manner as was seen with the lattice parameters (see Figure 3.1). This suggests that the

Figure 3.56. Energy of the ellipticity maximum as a function of the rare earth element. Error bars indicate the resolution of the measurement (0.1 eV).

shift in energy may be due to the decreasing size of the lattice parameters caused by the lanthanide contraction.

As was indicated earlier, the variation in the magnitude of the rotation may be related to the strengths of the magnetic moments on the manganese atoms. If this is true, the Kerr rotation should scale with the ratio of the manganese moment during the measurement to the manganese saturation moment. If one assumes a collinear arrangement of manganese and lanthanide elements, as was found in TbMn_6Sn_6 and HoMn_6Sn_6 [17], the Kerr rotation should scale linearly with the ratio of the magnetization to the saturation magnetization at a given temperature. This information is included in Table 3.2.

Figure 3.57 shows the height of the main structure in the Kerr rotation spectra plotted as a function of the fraction of saturation magnetization. The structure height, defined as the maxima in the Kerr spectra minus the minima in the Kerr spectra (independent of the energy), is shown because DyMn_6Sn_6 , GdMn_6Sn_6 , and TmMn_6Sn_6

Figure 3.57. Structure height as a function of fraction of saturation (see text for explanation). The line represents the linear regression of the data at 295K.

were measured with a slightly different setup, and their spectra are shifted vertically slightly. By plotting the structure height, the effects of this shift are eliminated. The data at 295K plot is linear, and a least squares fit line has a correlation coefficient of 0.96. This indicates that the magnitude of the rotation depends only on the magnitude of the moment on the manganese sublattice and is independent of the lanthanide element: if the samples were all saturated they would give identical results. It could also be said that the Kerr rotation for the entire series scales with the saturation magnetization the same as if it were a single compound. If the rotation did depend on the lanthanide moment, the data points from the different samples would not fall on a single line. This is true because each lanthanide element has a different saturation moment, and thus at a given percentage of saturation they would have different actual moments, and the rotation would depend on the product of the percentage of saturation and the saturation moment. It should be noted however, that the change in saturation magnetization across the series is small, so this relation may not be significant.

As explained earlier, the temperature dependence of the Kerr rotation can not be explained if the lanthanide moments contributed to the rotation because they increase by a factor of 2-3 as the temperature is decreased from 300K to 100K. As further evidence of this, measurements were made on TbMn_6Sn_6 at 200K and a range of applied magnetic fields. Using the slope of the linear M versus H curve and the linear θ_K versus H curve, the slope of the θ_K versus M curve was determined and is shown in Figure 3.57. The line is similar to the data points collected at room temperature; however, because the temperature is lower, the saturation moment on the manganese atoms is slightly higher, and thus the line has a slightly higher slope.

3.4. Corrosion Properties

There was no measurable change in the mass of a TmMn_6Sn_6 single crystal during the three months of exposure to the atmosphere indicating that little oxidation or corrosion had occurred. Table 3.3 gives the mass of the sample over the test period. There were no signs of corrosion seen on visual inspection.

Table 3.3. Corrosion data.

Days	Mass (g)
0	0.1521
1	0.1520
4	0.1521
7	0.1519
14	0.1520
25	0.1520
35	0.1519
63	0.1520
84	0.1519

4. CONCLUSIONS

Single crystals of the ternary compounds RMn_6Sn_6 , where $\text{R} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{and Lu}$, have been prepared by the flux growth technique. All of the compounds have the HfFe_6Ge_6 type crystal structure (space group $\text{P6}/\text{mmm}$), and the variation of the lattice parameters with lanthanide element exhibits the lanthanide contraction as well as evidence of crystal field effects.

Measurements on the magnetic properties of TbMn_6Sn_6 indicate that it orders ferrimagnetically at 450K. It undergoes a change in the easy axis from close to the c axis at low temperatures to in plane at higher temperatures. This transition occurs at 310K in zero DC field and can be shifted to lower temperatures by a field applied parallel to the a direction and to higher temperatures by a field applied parallel to the c direction.

HoMn_6Sn_6 orders ferrimagnetically at 400K, and it also undergoes a change in the easy axis between 150 and 225K with the moments located in the basal plane at high temperatures.

The magnetic properties of ErMn_6Sn_6 are more complex than the first two compounds. A magnetic phase diagram has been mapped out which shows that in a zero DC field the erbium sublattice orders antiferromagnetically at 65K and the manganese sublattice orders antiferromagnetically at 350K. When a sufficiently large DC field is applied, the manganese sublattice becomes ferromagnetic which causes the erbium sublattice to order ferromagnetically (and antiparallel to the manganese) due to the strong antiferromagnetic interaction between the manganese and erbium.

TmMn_6Sn_6 is similar to ErMn_6Sn_6 , yet there are distinct differences as seen by the magnetic phase diagram. In a zero DC field, the thulium and manganese sublattices order antiferromagnetically at 40K and 350K respectively. At low temperatures (below 100K), an applied DC field is able to flip the manganese moments and create a ferrimagnetic structure with a ferromagnetic manganese sublattice and a ferromagnetic thulium sublattice coupled antiparallel. At intermediate temperatures ($\sim 100\text{-}270\text{K}$), an applied field is only able to flip one-half of the moments.

LuMn_6Sn_6 orders antiferromagnetically near 400K. There is evidence of a partial spin flip transition as seen in TmMn_6Sn_6 ; however, it could not be well characterized due to the inability to saturate the moments even in an applied field of 9T.

in the *last para.* is across the entire series, it should also be noted that lattice parameters the manganese atoms order ferromagnetically. As one moves to smaller lattice parameters the interaction between manganese atoms becomes antiferromagnetic, and it becomes increasingly difficult to flip the moments into a ferromagnetic structure. This would seem to indicate that the Mn-Mn interaction is highly sensitive to the atomic spacings and that ErMn_6Sn_6 has a structure such that it is close to the crossover point.

The structure of the room temperature magneto-optic spectra for RMn_6Sn_6 with $\text{R} = \text{Gd-Tm}$ are all similar. The maximum Kerr rotation found was 0.225 degrees in TbMn_6Sn_6 , and the magnitude of the maximum Kerr rotations scaled across the series as a function of the fraction of saturation. This, combined with the temperature dependence, indicates that the Kerr rotation is primarily a function of the manganese moment and is independent of the lanthanide element present. The main features of the spectra shift to slightly higher energies as one moves from gadolinium to thulium. This may be related to the contraction in the lattice parameters. The materials show good corrosion resistance in normal atmospheric conditions.

good

REFERENCES CITED

- [1] K.A. Gschneidner, Jr., and A.H. Daane, in: K.A. Gschneidner, Jr., and L. Eyring (eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 11, North-Holland, Amsterdam, 1998, p. 409.
- [2] K.A. Gschneidner, Jr., Journal of Alloys and Compounds 192 (1993) 1.
- [3] K.A. Gschneidner, Jr., Journal of the Less Common Metals 114 (1985) 29.
- [4] K.H.J. Buschow, in: E.P. Wohlfarth and K.H.J. Buschow (eds.), Ferromagnetic Materials, ch. 5, Elsevier, The Netherlands, 1988, p. 493.
- [5] D.C. Jiles, Magnetism and Magnetic Materials, Chapman and Hall, New York, 1991.
- [6] J. Schoenes, in: K.H.J. Buschow et al. (eds.), High Density Digital Recording, ch. 13, Kluwer Academic Publishers, The Netherlands, 1993, p. 377.
- [7] R. Pittini, J. Schoenes, O. Vogt, and P. Wachter, Phys Rev. Lett. 77 (1996) 944.
- [8] G.Q. Di, S. Iwata, and S. Uchiyama, Journal of Magnetism and Magnetic Materials 131 (1994) 242.
- [9] J.X. Shen, R.D. Kirby, D.J. Sellmyer, and Y.J. Wang, J. Appl. Phys 69 (1991) 5984.
- [10] Fang Rui-yi, Dia Dao-sheng, Zhang Sheng, Long Pin, Ma Ting-jun, Dia Chen, Zhang Xu-xin, Journal of Magnetism and Magnetic Materials 104-07 (1992) 1031.
- [11] J. Schoenes, in: K.H.J. Buschow (eds.), Electronic and Magnetic properties of Metals and Ceramics, vol. 3A, ch. 2, VCH, Weinheim, Germany, 1991, p147.
- [12] F. Weitzer, A. Leithe-Jasper, K. Hiebl, P. Rogl, Qian Qi, and J. M. D. Coey, J. Appl. Phys. 73 (1993) 8447.
- [13] F. Weitzer and P. Rogl, Journal of Phase Equilibria 15 (1993) 636.
- [14] B. Malaman, G. Venturini, and B. Roques, Mat. Res. Bull. 23 (1988) 1629.
- [15] G. Venturini, B. Chafick El Idrissi, and B. Malaman, J. Mag. Magn. Mat. 94 (1991) 35.

- [16] Jifan Hu, Kai-Ying Wang, Bo-Ping Hu, Yi-Zhong Wang, Zhenxi Wang, Fuming Yang, Ning tang, Ruwen Zhao, and Weidong Qin, J. Phys. Condes. Matter 7 (1995) 889.
- [17] B. Chafik El Idrissi, G. Venturini, B. Malaman, and D. Fruchart, Journal of the Less-Common Metals 175 (1991) 143.
- [18] G. Venturini, D. Fruchart, and B. Malaman, Journal of Alloys and Compounds 236 (1996) 102.
- [19] G. Venturini, R. Welter, and B. Malaman, Journal of Alloys and Compounds 200 (1993) 51.
- [20] P.C. Canfield and Z. Fisk, Philosophical Magazine B 65 (1992) 1117.
- [21] Lakeshore 7000 Series System Users Manual, Lake Shore Cryotronics, Inc., Westerville, Ohio, 1992.
- [22] Oxford MagLab 2000 Users Manual, Oxford Instruments (UK), Oxon, England, 1997.

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