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Magnetic and magneto-optical properties of $\text{Mn}_5(\text{Ge}_{1-x}\text{M}_x)_3$ alloys with $\text{M}=$Sn, Pb

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We report on the magnetic and magneto-optical properties of the intermetallic alloys $\text{Mn}_5(\text{Ge}_{1-x}\text{M}_x)_3$, where $\text{M}=$Sn, Pb. Generally, these alloys were ordered ferromagnetically at $T>300$ K for $x<0.3$. The structure of $\text{Mn}_5(\text{Ge}_{1-x}\text{Sn}_x)_3$ remains in the hexagonal $\text{Mn}_5\text{Si}_3(hP16)$ phase up to $x=0.25$ and then changes to $\text{Ni}_5\text{In}(hP6)$ as $x$ approaches 1. The magnetization and Curie temperature of these alloys is largest for small $x$ and reach a minimum value near $x=0.5$. The room temperature Polar Kerr rotation, however, increases from $-0.06^{\circ}$ at $x=0$ to maximum value of $-0.12^{\circ}$ at $x=0.1$ before decreasing toward zero for $x>0.3$. The $\text{Mn}_5(\text{Ge}_{1-x}\text{Pb}_x)_3$ samples show a $\text{Mn}_5\text{Si}_3$ structure with ferromagnetic behavior for $x<0.3$, and varying structure with rapidly decreasing magnetization above $x=0.3$. The magnetic behavior observed was complex for $x>0.3$.

The Kerr rotation of the Pb-doped alloys in the ferromagnetic region monotonically decreases from $-0.06^{\circ}$ to zero at $x=0.3$.

I. INTRODUCTION

Current research of materials for use as magneto-optic storage media focuses on ferromagnetic materials that have strong uniaxial anisotropy and Curie temperatures in the range of 30–200 °C. The intermetallic compound $\text{Mn}_5\text{Ge}_3$ is ferromagnetic with a Curie temperature in the range of 27–47 °C. Favorable optical properties such as high optical absorption and large Kerr rotation might be expected largely due to the metallic character of the alloy and the high density of ferromagnetically aligned $\text{Mn}^{2+}$ and $\text{Mn}^{3+}$ ions present. Panissod and his coworkers have studied the magnetic and magneto-optical properties of the intermetallic alloys $\text{Mn}_5(\text{Ge}_{1-x}\text{M}_x)_3$, where $\text{M}=$Sn, Pb. Generally, these alloys were ordered ferromagnetically at $T>300$ K for $x<0.3$. They reported that Si can be substituted for Ge in $\text{Mn}_5\text{Ge}_3$ over the whole range of $x$ and that these alloys are isostructural ($D8_a$). The transition is from ferromagnetic for $x<0.85$ to antiferromagnetic for $x>0.85$. The aim of this work is to study the effects of heavy-element alloying on the magnetic properties and magnitude of the Kerr rotation ($\Theta_K$). We report on the preparation and properties of the compounds $\text{Mn}_5(\text{Ge}_{1-x}\text{M}_x)_3$ with $\text{M}=$Sn, Pb.

II. EXPERIMENTS

Samples were prepared from 99.995 at. % pure Mn, 99.99 at. % pure Ge, and 99.9999 at. % pure Sn or 99.999 at. % pure Pb. Stoichiometric amounts were alloyed by arc melting in an argon atmosphere. In order to obtain homogeneous alloys, each sample was melted four to five times. Mass losses during melting totaled about 2% for $\text{Mn}_5(\text{Ge}_{1-x}\text{Sn}_x)_3$ and about 3% for $\text{Mn}_5(\text{Ge}_{1-x}\text{Pb}_x)_3$. The samples were then annealed in vacuum at 700 °C for 10 days.

The structure of the samples was analyzed by x-ray diffraction. Their magnetization and coercivity were measured using an alternating gradient force magnetometer (AGFM) and superconducting quantum interference device (SQUID). The Curie temperatures were measured by both a high-temperature Faraday balance magnetometer and AGFM at $H=500$ Oe. The Polar Kerr rotation was determined by a home-made apparatus at room temperature and fields up to 8 kOe.

III. RESULTS AND DISCUSSION

A. Crystallographic data

Figure 1 shows x-ray diffraction measurements on representatives of the $\text{Mn}_5(\text{Ge}_{1-x}\text{Sn}_x)_3$ samples. $\text{Mn}_5(\text{Ge}_{0.95}\text{Sn}_{0.05})_3$ [Fig. 1(a)] is found to have a $\text{Mn}_5\text{Si}_3(hP16)$ type structure, as does $\text{Mn}_5(\text{Ge}_{0.70}\text{Sn}_{0.30})_3$ [Fig. 1(b)] but with a $\text{Ni}_5\text{In}(hP6)$ structure phase also beginning to appear. The $\text{Mn}_5(\text{Ge}_{0.50}\text{Sn}_{0.50})_3$ sample [Fig. 1(c)] shows the $\text{Ni}_5\text{In}(hP6)$ structure. Only small amounts of Mn oxides show up in the x-ray spectra. It has also been found by others that $\text{Mn}_5\text{Ge}_3$ has a $\text{Mn}_5\text{Si}_3$ structure and $\text{Mn}_5\text{Sn}_3$ has a $\text{Ni}_5\text{In}$ structure. When Sn is substituted for Ge in $\text{Mn}_5\text{Ge}_3$ [i.e., $\text{Mn}_5(\text{Ge}_{1-x}\text{Sn}_x)_3$] it can be expected that for small $x$ the compounds will maintain the $\text{Mn}_5\text{Si}_3$ structure and that for large $x$ the compounds should form the $\text{Ni}_5\text{In}$ structure. In the middle range these structures could be mixed and show various lattice distortions. Since the Sn atomic diameter is larger than that of Ge, when Sn is substituted for Ge in $\text{Mn}_5\text{Ge}_3$, the lattice parameter of the crystal changes. Table I gives the variations in the lattice parameters measured in our samples.

Figure 2 shows x-ray diffraction measurements on some of the $\text{Mn}_5(\text{Ge}_{1-x}\text{Pb}_x)_3$ samples. We find that, as expected, $\text{Mn}_5(\text{Ge}_{0.95}\text{Pb}_{0.05})_3$ [Fig. 2(a)] has the $\text{Mn}_5\text{Si}_3(hP16)$ structure. This structure type becomes unstable at $x>0.3$. $\text{Mn}_5(\text{Ge}_{0.50}\text{Pb}_{0.50})_3$ [Fig. 2(b)] shows the $\text{Ni}_5\text{Sn}(hP8)$ type structure, which is predominant for this composition. $\text{Mn}_5(\text{Ge}_{0.25}\text{Pb}_{0.75})_3$ [Fig. 2(c)] mainly shows the $\text{Ni}_5\text{Sn}(hP8)$ type structure but broad peak is found at a position expected from a pure tetragonal Mn phase. We also note that for $x$ larger than 0.5 the desired compounds were difficult to form. This was especially noted for $\text{Mn}_5\text{Pb}_3$, which often resulted.
in a fcc Pb structure with the main peak from the $\beta$-Mn spectrum also present. Mn has a smaller atomic diameter than Pb so it is expected that Mn$_3$Pb$_3$ in a fcc phase have a smaller lattice parameter than the pure fcc Pb lattice. These effects of alloy substitutions are confirmed by our experimental results. As shown in Table I, we found that the cubic lattice parameter $a$ changes from 4.962 Å for the pure Pb crystal to 4.955 Å for the Mn$_3$Pb$_3$ alloy.

TABLE I. Structural lattice parameters for the relevant compositions of Mn$_3$(Ge$_{1-x}$Sn$_x$)$_3$ for M=Sn, Pb, and the average magnetic moment per Mn atom at $T=5$ K. Data are only shown for samples from which it could be clearly calculated.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice parameter $a$ (Å)</th>
<th>Average moment per Mn atom ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_3$Ge$_3$</td>
<td>7.193</td>
<td>2.52</td>
</tr>
<tr>
<td>Mn$<em>3$(Ge$</em>{0.5}$Sn$_{0.5}$)$_3$</td>
<td>7.106</td>
<td>2.52</td>
</tr>
<tr>
<td>Mn$<em>3$(Ge$</em>{0.33}$Sn$_{0.67}$)$_3$</td>
<td>7.176</td>
<td>2.33</td>
</tr>
<tr>
<td>Mn$<em>3$(Ge$</em>{0.25}$Sn$_{0.75}$)$_3$</td>
<td>7.116</td>
<td>2.23</td>
</tr>
<tr>
<td>Mn$<em>3$(Ge$</em>{0.17}$Sn$_{0.83}$)$_3$</td>
<td>7.172</td>
<td>2.13</td>
</tr>
<tr>
<td>Mn$_3$Ge$_3$</td>
<td>7.193</td>
<td>2.52</td>
</tr>
<tr>
<td>Mn$<em>3$(Ge$</em>{0.9}$Pb$_{0.1}$)$_3$</td>
<td>7.179</td>
<td>2.42</td>
</tr>
<tr>
<td>Mn$<em>3$(Ge$</em>{0.8}$Pb$_{0.2}$)$_3$</td>
<td>7.164</td>
<td>2.16</td>
</tr>
<tr>
<td>Mn$<em>3$(Ge$</em>{0.6}$Pb$_{0.4}$)$_3$</td>
<td>7.168</td>
<td>2.10</td>
</tr>
<tr>
<td>Mn$<em>3$(Ge$</em>{0.4}$Pb$_{0.6}$)$_3$</td>
<td>6.755</td>
<td>1.23</td>
</tr>
<tr>
<td>Mn$_3$Pb$_3$</td>
<td>4.955</td>
<td>0.01</td>
</tr>
<tr>
<td>Pb</td>
<td>4.963</td>
<td>0.00</td>
</tr>
</tbody>
</table>

B. Magnetic properties

Figure 3(a) shows the compositional dependence of the magnetization measured at $T=5$ K and a maximum field of 50 kOe with a SQUID magnetometer. The Curie temperatures for the compounds studied are shown in Fig. 3(b). All of the Mn$_3$(Ge$_{1-x}$Sn$_x$)$_3$ alloys made have a ferromagnetic transition and for $x \leq 0.3$ they are ferromagnetic at room temperature. The magnetization at $T=5$ K first generally decreases with increasing $x$, and then shows a slow increase above $x=0.5$. The coercivity however is maximized for $x=0.5$, reaching 1.2 kOe at $T=5$ K. The Curie temperature initially remains nearly constant, then decreases with increasing $x$ beyond $x=0.3$, reaching a minimum at $x=0.5$, after which it increases again as $x$ goes to 1.0.

It can be seen in Table I that as $x$ increases, both the lattice parameter $a$ and the average moment per Mn atom generally decrease. This is understandable since the hybridization of Mn 3$d$ electronic states normally increases as the interatomic separation becomes smaller as given by the quantum theory.
The Mn$_5$(Ge$_{1-x}$Pb$_x$)$_3$ alloys are ferromagnetic at room temperature only for $x < 0.2$. The magnetization and Curie temperature show a minimum at $x = 0.05$, for reasons that are not presently clear. When $x > 0.1$ both of these properties decrease as $x$ increases. The explanation is the same as given for the Mn$_5$(Ge$_{1-x}$Sn$_x$)$_3$ alloys concerning the hybridization of the Mn 3d states. When $x > 0.3$ the Pb substituted alloys show a complex magnetic behavior. For example, the Mn$_5$(Ge$_{0.85}$Pb$_{0.15}$)$_3$ sample measured at $T = 5$ K and up to $H = 50$ kOe has a small (about 1.5 emu/g) magnetization which is unsaturated, and a coercivity of about 11 kOe, while at room temperature it still has a coercivity of about 2 kOe.

C. Magneto-optic properties

Figure 3(c) shows the relationship of the magnitude of the Polar Kerr rotation to the composition, measured at room temperature in fields up to 8 kOe. The sign of the rotation is negative for all of the samples studied. For Mn$_5$(Ge$_{1-x}$Pb$_x$)$_3$, the Kerr rotation monotonically decreases from the value for the parent alloy Mn$_5$Ge$_3$ with increasing $x$. In agreement with the magnetization at room temperature with an applied field of 8 kOe the Kerr rotation of the Sn substituted compounds increased slightly for $x < 0.15$. The peak value of $\theta_K = 0.12^\circ$ at $x = 0.1$ is enhanced above what would be expected from a direct relationship between $\theta_K$ and $M$. Beyond this peak the Kerr rotation drops off, going to zero rapidly outside the single phase region at $x = 0.25$. The Kerr rotation values below $x = 0.4$ for both cases was measured very near the Curie temperature in both series of samples which would adversely affect the magnitude of the rotation due to decreased magnetic magnetizations. However, the Polar Kerr rotation is an intrinsic quantity that depends on factors such as composition, crystal structure, and electronic structure. It is interesting that there is an enhanced maximum in $\Theta_X$ for the Sn case that apparently occurs within a single phase region. Presumably this reflects subtle changes in the electronic structure. This indicates the need for at least a spin-polarized calculation on the parent Mn$_5$Ge$_3$ compound.

IV. CONCLUSION

The magnetic and magneto-optical properties strongly depend on the alloy structure. Our Mn$_5$(Ge$_{1-x}$Pb$_x$)$_3$ samples showed the Mn$_5$Si$_3$ structure and were ferromagnetic for $x < 0.3$, exhibiting complex magnetic behavior for $x > 0.3$. All of the Mn$_5$(Ge$_{1-x}$Sn$_x$)$_3$ alloys were also ferromagnetic, but the low-temperature magnetization showed a minimum value at $x = 0.5$. Only the substitution of Sn for Ge in Mn$_5$Ge$_3$ allowed the alloy to both keep the Mn$_5$Si$_3$ structure and increase the Kerr rotation.

In general the presence of heavy elements is necessary for large spin-orbit interactions, which can aid in producing a large Kerr effect; in the case of these compounds there is a compensating effect on alloying with Sn or Pb that reduces the strength of the magnetic coupling, as evidenced by a reduction in $M_r$ and $T_c$. Thus, in these compounds, any tendency for Kerr-effect enhancement is overwhelmed by the destruction of the ordered magnetic state.

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