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Magnetic properties of low-moment ferrimagnetic Heusler Cr$_2$CoGa thin films grown by molecular beam epitaxy

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Spin gapless semiconductors (SGS) have been predicted to merge the properties of gapless semiconductors and half-metallic magnets, which would be beneficial in various magnetoelectronic applications. The schematic of the density of states (DOS) is seen in Fig. 1(a), where the spin up (orange) band is the majority state and the spin down (green) band is the minority state, and the Fermi energy ($E_F$) is placed so that the majority band acts as a gapless semiconductor. However, for high density spintronic technologies, a low magnetic moment is preferable in order to minimize interactions while maintaining spin polarization as in the case of Mn$_2$Ru$_2$Ga. Binary V$_3$Al with a Heusler structure has been synthesized in bulk and has been shown to be a traditional G-type Néel antiferromagnet with two identical compensating vanadium moments, and therefore, does not have the ability to be spin polarized due to its symmetrical density of states.

Cr$_2$CoGa has been predicted to be an inverse Heusler half-metallic compound with low net moment equal to 0.09 $\mu_B$ per formula unit (f.u.), but large Curie temperature between 1300 and 1600 K. The inverse Heusler (XA) phase has a space group F43m, which varies slightly from the full Heusler (L2$_1$) phase with space group Fm3m, seen in Fig. 1(b). The difference between the two structures leads to an obvious change in the body diagonal along the ⟨111⟩ direction, indicated by a bold line in Fig. 1(b). The L2$_1$ structure has an atomic configuration of X-Y-Y-Z along the ⟨111⟩ diagonal, whereas the XA structure has X-X-Y-Z. The activation energy for the formation of Cr$_2$CoGa in the XA lattice is lower than the L2$_1$ structure; however, the activation energy is still positive ($+0.08$ eV/f.u. and $+0.7$ eV/f.u., respectively), indicating that phase segregation will occur for equilibrium conditions. Cr$_2$CoGa with phase segregates was previously synthesized by Feng et al. using molecular beam epitaxy (MBE) at 450 °C. In the present study, singular phase inverse Heusler Cr$_2$CoGa thin films were achieved via MBE growth without phase segregation using molecular beam epitaxy. The present as-grown films exhibit a low magnetic moment from antiferromagnetically coupled Cr and Co atoms as measured with superconducting quantum interface device magnetometry and soft X-ray magnetic circular dichroism. Electrical measurements demonstrated a thermally-activated semiconductor-like resistivity component with an activation energy of 87 meV. These results confirm spin gapless semiconductor behavior, which makes these thin films well positioned for future devices. Published by AIP Publishing.
The XRD diffractograms of Cr$_2$CoGa are seen in Fig. 2, where the as-grown sample (a300) shows (002), (004), and (420) peaks that are consistent with the inverse Heusler lattice marked with purple lines. The left inset of Fig. 2 shows the RHEED pattern of the as-grown sample after growth, which shows partial epitaxial alignment on the (001) plane, indicating ordered polycrystallinity causing unique texturing of the sample. This strong texturing can account for lack of an ordered polycrystallinity causing unique texturing of the sample.

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For annealing at 325 °C, then decreases to $\mu = 0.2 \mu_B$/f.u. for annealing at 400 °C. The decrease in moment is attributed to a decrease in Cr$_2$CoGa fraction from phase segregation as indicated in the XRD. These hysteresis loops also indicate a magnetic anisotropy as seen by the small difference in the approach to saturation for fields applied parallel and perpendicular relative to the film surface. At low fields, the moment approaches saturation more quickly for the perpendicular orientation due to shape anisotropy. This anisotropy is expected and is a sign of texturing. The magnetization was also measured as a function of temperature, $\mu(T)$, and field direction. Figure 3(c) displays $\mu(T)$ between 5 and 400 K for the three samples at $\mu_0 H = 0.09$ T, showing that the material has a large Curie temperature, $T_C$ greater than 400 K. The $\mu(T)$ data was fit to the mean field model $\mu(T) = \mu_s(1 - \frac{T}{T_C})^\gamma$, where $\gamma$ is a fitting parameter on the order of $\gamma \sim \frac{1}{2}$. Table I lists the results of the fits, where $T_C$ monotonically decreases from 750 to 440 K for increasing annealing temperature. Interestingly, for fields applied perpendicular to the film the $\mu(T)$ data show the differences for field cooling (FC) and zero-field cooling (ZFC), where the ZFC data shows maxima in the 100–200 K range. This behavior can be attributed to nanoscale magnetic domain structure. The perpendicular magnetization data indicates that the thin films have some superparamagnetic behavior, with a blocking temperature of $T_B \approx 150$ K.

The total atomic moments of Cr and Co were measured through analysis of the X-ray absorption spectroscopy (XAS) taken at the L$_3$ and L$_2$ edges with circularly polarized X-rays. In Fig. 3, the XAS measurements of the Cr (d upper) and Co (e upper) L$_3$ and L$_2$ edges are plotted as a function of energy. There are noticeable changes in the Cr XAS spectra as a function of annealing. The as-grown sample (a300) has a valence occupancy of Cr$^{3.1+}$, obtained by considering previous modeling of the Cr d-orbitals. The valence then increases to Cr$^{3.4+}$ when annealed to 325 °C, and finally to Cr$^{4.7+}$ when annealed to 400 °C. Therefore, the Cr occupancies are changing as a function of annealing, indicating that there is phase segregation occurring at the higher annealing temperatures. The Co L-edges have a relatively constant valence Co$^{3.3}$ and orbital configuration of (3d$^6$) as a
function of annealing. XMCD measurements were taken using opposite circular polarization and using positively and negatively applied fields in order to obtain XMCD spectra for the Cr (d lower) and Co edges (e lower), seen in Fig. 3. The Cr signal was quite low due to the antiferromagnetically coupled Cr atoms, and there was a branching ratio of \( L_3/L_2 = 1.53 \). The extracted magnetic moments are plotted in Fig. 3(f), where the Co atomic moment increases by a factor of 7 between the temperatures 300 and 325 \(^\circ\)C, further indicating phase segregates formed from the Heusler lattice after annealing at 325 \(^\circ\)C. The increasing magnetic moment supports the possible XRD phase segregations with an increasing Co phase concentration. Table I lists the magnetic moments measured using SQUID magnetometry and the XMCD-extracted Cr and Co magnetic moments as a function of annealing. The SQUID magnetic moments are quite low, between 0.21 and 0.46 \( \mu_B/f.u. \), while the magnetic moment of the Co atoms is quite large in comparison. These differences increase for increasing annealing temperatures. The difference in the moments resides primarily in the increasing moment on the Co atoms. These phase decompositions would have a large Co moment; however, the magnetic moment of the Cr would remain low due to its antiferromagnetic properties, which supports the low XMCD magnetic moment of Cr. Due to the structural disorder in the thin film, the magnetic moment is larger than the predicted 0.09 \( \mu_B/f.u. \) and has increased to 0.46 \( \mu_B/f.u. \).

The electrical properties of a Cr\(_2\)CoGa film were measured as a function of temperature. The room temperature resistivity was found to be \( \rho_{300} = 90 \) \( \mu \Omega \) cm. Figure 4 shows that the temperature-dependent resistivity is metallic-like, but is composed of temperature-independent and temperature-dependent contributions \( \rho = \rho_0 + \rho(T) \). The temperature dependent contribution \( \rho(T) \) is seen to be linear with \( T \) only over an intermediate range 50–200 K, where the carrier concentration is constant and mobility is affected by phonon scattering. It becomes sublinear above 200 K, due to an increase in the number of carriers. For this semiconductor-like activation of carriers where \( \rho(T) \) can be fit to

\[
\frac{1}{\rho_{xx}}(T) = \sigma_{xx}(T) = n_m e \mu_{ph}(T) + n_0(T) e \mu_a,
\]

where \( 1/\mu_{ph}(T) = c T + 1/\mu_0(T = 0) \), \( c T \) is due to carrier-phonon scattering, and \( n_m \) is the number of metallic carriers.

### Table I

<table>
<thead>
<tr>
<th>Temperature ( T_{\text{anneal}} ) ((^\circ)C)</th>
<th>( M_s ) (( \mu_B/f.u. ))</th>
<th>Cr (( \mu_B ))</th>
<th>Co (( \mu_B ))</th>
<th>Curie temperature ( T_C ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.46</td>
<td>-0.18</td>
<td>0.47</td>
<td>750</td>
</tr>
<tr>
<td>325</td>
<td>0.57</td>
<td>-0.29</td>
<td>1.5</td>
<td>640</td>
</tr>
<tr>
<td>400</td>
<td>0.21</td>
<td>0</td>
<td>2.2</td>
<td>440</td>
</tr>
</tbody>
</table>
When the sample was annealed above 300 °C, the structural properties of the lattice showed a slight tetragonal distortion, and the films grew partially oriented relative to the GaAs substrate. The number of thermally activated carriers in the second term varies as \( n_e(T) = \exp(-\Delta/T) \) with activation temperature \( \Delta \). The activation energy of the carriers was found to be 87 meV, which is on the same order as SGS Mn2CoAl\(^{30,31}\) and Ti2MnAl.\(^{31}\) The anomalous Hall effect (AHE) behavior shown in the inset of Fig. 4 reflects the measured magnetization seen in Fig. 3(b). The AHE conductivity was found to be \( \sigma_{xy} = 50 \text{ S/cm} \), a small value consistent with other SGS materials and arises from intrinsic Berry phase curvature.\(^{5,6,30-33}\) The as-grown Cr2CoGa exhibits SGS behavior identified by the small AHE coefficient and the small activation energy characteristic of a low energy band gap.\(^{30,32,33}\)

The magnetic properties of MBE-grown Cr2CoGa thin films were investigated as a function of annealing. RHEED monitoring (see Fig. 2 left inset) indicated that the Cr2CoGa grew partially oriented relative to the GaAs substrate. The structural properties of the lattice showed a slight tetragonalization of the lattice parameters in the as-grown sample. When the sample was annealed above 300 °C, peaks that were unrelated to the Heusler structure appeared in the diffractogram indicating phase segregation. Magnetic measurements indicated that the as-grown lattice has a low total magnetic moment (0.5 \( \mu_B/\text{f.u.} \)); however, the magnetic moment varied as the phase becomes segregated. The XAS spectra further supported the phase segregation of the lattice, since the valence states of the Cr changes visibly as a function of annealing. Nevertheless, the as-grown samples did exhibit the Heusler structure and revealed a low magnetic moment with antiferromagnetically coupled Cr and Co atoms. The as-grown sample exhibited SGS electrical properties that could be utilized in future devices.

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