Coexistence of Ferromagnetic and a Re-entrant Cluster Glass State in the Layered Quaternary \((\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}\)

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Herein we present evidence for the coexistence of a Mn-rich ferromagnetic (FM) state and a Mn-poor reentrant cluster glass state in bulk, polycrystalline, layered \((\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}\) samples, where \(x\) is varied between 0.01 and 0.1. The Mn-poor regions form a reentrant cluster glass state below \(\sim 30\) K. The Mn-rich regions become FM at Curie temperatures that increase with increasing Mn content. The interface coupling between these two regions gives rise to exchange anisotropy and a change in sign at 20 K resulting in, rarely observed, inverted hysteresis loops.

Keywords: MAX Phase, Cluster Glass, Inverted Loops

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The \(M_{n+1}AX_n\) (MAX) phases—where M is an early transition metal, A is an A group element—mostly from groups 13 and 14—and X is carbon and/or nitrogen and \(n = 1\) to 3—are a large (>60) family of thermodynamically stable nanolaminates, wherein \(M_{n+1}X_n\) layers are interleaved with layers of pure A, with the X atoms occupying the octahedral sites between the M layers.[1] These phases, most of which were discovered by Nowotny et al.[2] in the 1960s, have attracted much interest recently since some of them exhibit a unique combination of properties, such as high thermal stability, excellent thermal and electrical conductivities, together with excellent machinability,[1,3] fully reversible dislocation-based deformation,[4] among other attributes.

Materials with inhomogeneities at the nanoscale are of fundamental interest as well as in applications. Disorder arises when the energy differences between the different ordered states is small.[5] Furthermore, magnetically, the interplay of different coexisting states can give rise to exotic magnetic states. This interplay is particularly important in multilayered structures that, for the most part, are artificially produced.[6]

With the substantial interest generated by magnetic multilayered structures and the importance of interfaces in these structures, the allure, and potential, of magnetic MAX phases, that are intrinsically nanolaminated, is obvious. The quest for magnetic MAX phases, led by Rosén and coworkers, is a few years old.[7–11] Starting with a theoretical paper predicting the existence of a stable magnetic \((\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}\) compound, wherein nonmagnetic Cr layers, form an inherent structure of atomically thin, magnetic multilayers.[7] In that paper, it was also suggested that the degree of disorder between the Cr and Mn atoms in the compound could be used to tune the sign and magnitude of their coupling. In subsequent papers, it was theoretically shown that the most promising MAX phases are ones in the Cr–Mn–A–C system, were A is Al, Ga or Ge.[8–11] It was only recently, however, that Ingason et al., showed that \((\text{Cr}_{1-x}\text{Mn}_x)_2\text{GeC}\) thin films were ferromagnetic (FM) with Curie temperatures,
Based on DC magnetization measurement, it was concluded that the Mn atoms were disordered. Nevertheless, from the first principle calculation, the energy difference between the FM-ordered state and antiferromagnetic (AFM) disordered state was quite small, suggesting that they could co-exist.[7]

The powders used herein were graphite (99.9%, Cr (99.5%), Ge (99.99%) (Research Institute for Nonferrous Metals) and Mn (99%) Aladdin Industrial Inc.) To obtain the (Cr$_{1-x}$Mn$_x$)$_2$GeC polycrystalline samples, with $x = 0.01, 0.02, 0.05$ and 0.1 stoichiometric amounts were mixed in an agate mortar and sealed in evacuated quartz tubes, heated to 1100°C and held at that temperature for 48 h. After furnace cooling, the samples were ground, pelletized, cold isostatically pressed to a pressure of 160 MPa, re-sealed in evacuated quartz tubes and annealed again at 1200°C for another 72 h.

The samples were characterized with X-ray powder diffraction, XRD. DC magnetization measurements were performed with a quantum design superconducting quantum interference device. AC magnetization measurements were carried out on a quantum design physical property measurement system.

All major peaks in the XRD patterns of the as prepared samples belonged to the MAX phase (Figure 1). For the $x = 0.1$ sample, a few small peaks belonging to Cr$_2$Ge$_2$C$_3$ were also observed (Figure 1). The $a$- and $c$-lattice parameters are calculated to be 2.953 and 12.086 Å, respectively. These values are quite similar to those of pure Cr$_2$GeC, with $a$- and $c$-lattice parameters of 2.954 and 12.08 Å, respectively.[16] In accordance with the result of Ingason et al., the incorporation of Mn into Cr$_2$GeC does not appear to affect the lattice parameters.[10] In Nakamura et al.’s recent work,[15] they found a nonlinear dependence of the lattice parameters on Mn content. For reasons that are unclear, however, their lattice constants in general, and those for pure Cr$_2$GeC ($a \approx 3.05$ Å and $c \approx 12.5$ Å) in particular are significantly higher than the reported values for Cr$_2$GeC ($a \approx 2.95$ Å, $c \approx 12.08$ Å),[16] and our results.
Figure 2. (a) Temperature dependence of zero field, ZFC, and field cooled, FC, DC magnetization curves for (Cr$_{1-x}$Mn$_x$)$_2$GeC as a function of $x$. (b) Temperature dependence of zero field, ZFC, and field cooled, FC, DC magnetization curves for (Cr$_{0.95}$Mn$_{0.05}$)$_2$GeC as a function of cooling rate/ quenching. The applied magnetic field was $5/4\pi 10^3$ Am$^{-1}$ for (a) and (b). Inset in (b) shows the magnetization for (Cr$_{0.95}$Mn$_{0.05}$)$_2$GeC synthesized at 1000 $^\circ$C in an applied field of $5/4\pi 10^5$ Am$^{-1}$.

The dependencies of the magnetization, $M$, on temperature and composition, under ZFC and field cooled (FC) modes in an applied field, of $5/4\pi 10^3$ Am$^{-1}$ are shown in Figure 2(a). The $x = 0.01$ sample shows a reentrant cluster glass-like transition at 32.7 K; with increasing Mn content, an additional higher temperature transition appears. For the $x = 0.02$ and $x = 0.05$ samples, two transitions are evident: one at low temperature identical to the $x = 0.01$ sample, the others at $\sim 120$ and at 286 K, respectively. For the $x = 0.1$ sample, the higher temperature transition is observed at 320 K, the lower temperature transition is not observed, but the cluster glass transition is still present. It is important to note that the fact that $T_c$ is a function of Mn content rules out the possibility that the signal is coming from a magnetic impurity phase that in principle would possess a $T_c$ that was independent of composition. In this case, the increases in $T_c$ with Mn content most probably reflect a stronger interaction between the Mn atoms as the average distance between them shrinks (compare Figure 3(b) and 3(c)). In Figure 3, the Mn moments are assumed to lie in the basal plane because they do so in Mn$_2$GaC.[14] The actual situation is most probably significantly more complicated.[10] It is worth noting that although some theoretical calculation indicate that the undoped Cr$_2$GeC may have an AFM ground state,[17–19] Cr$_2$GeC, like other MAX phases [1] appears to be a typical Pauli paramagnetic solid.[15]

To further check the validity of this conclusion, a sample with $x = 0.05$, was quenched from 1100 $^\circ$C into water and its magnetization was measured. In this case, the high temperature $T_c$ was significantly suppressed (Figure 2(b)), confirming the importance of having a critical Mn concentration for the high temperature or Mn-rich FM transition. Noteworthy, and consistent with this interpretation, is the large increase in the spin glass signal observed after quenching (Figure 2(b)).

What this result also strongly implies is a phase separation of the Mn atoms into Mn-rich and Mn-poor regions (Figures 2(a) and Figure 3(d)). The Mn-rich regions exhibit the higher ordering temperature that, as noted above, is a function of Mn content. The Mn-poor layer, on the other hand, orders at $\approx 30$ K. Presumably, for the $x = 0.1$ sample, the Mn content is larger than the percolation threshold which in turn results in the formation of a more homogeneous material that exhibits a single transition (Figure 2(a)). At this time, the Mn segregation mechanism is unclear. First principles calculations indicate that the Mn–C–Mn configuration is energetically more favorable compared to the Mn–C–Cr configuration.[10] Furthermore, given the continuous and gradual changes in lattice parameters of the solid solutions, it is not unreasonable to assume that spinodal
decomposition is occurring. This comment notwithstanding, more work is needed to better understand this crucial experimental variable.

The importance of this variable, however, is manifested in the actual $T_c$ values in the Nakamura et al. paper,[15] the $T_c$ values are lower than those presented herein. For example, their $T_c$ at $x = 0.2$ is 270 K; herein, $T_c$ at the lower Mn loading of 0.1 is 320 K. The only apparent difference is the synthesis temperature. We also note that the synthesis temperature is essential for a higher $T_c$. For example a $x = 0.05$ sample synthesized at 1000°C shows a transition at ~224 K (inset of Figure 2(b)). This fact may relate to the formation of Mn-rich regions at elevated temperature. In our own study when $x \geq 0.2$, a substantial amount of impurity, most probably (Mn$_{1-x}$Cr$_x$)$_5$Ge$_3$, emerged and the diffraction pattern was identical to the impurity phase in Figure 1 of Ref. [15]. The $x = 0.2$ sample in our own work showed a sharp transition at 250 K. It is reasonable to conclude that the Mn containing intermetallic is responsible for the magnetism observed in the $x > 0.2$ sample.

For both the 0.02 and 0.05 compositions, below the 32 K transition, the ZFC magnetization curve shows a broad maximum at ~22 K. Cooling below 10 K results in a drop in magnetization (Figure 2(a)), suggesting the existence of a spin cluster glass behavior at the lowest temperatures.[20]

To investigate the nature of this low temperature transition, AC-susceptibility measurements for the $x = 0.05$ sample were performed as a function of temperature from 3 to 350 K in an applied field of $5/4\pi 10^3$ Am$^{-1}$. The prominent frequency independent peak at 22.5 K (Figure 4(a)) agrees well with the maximum in DC magnetization observed at ~22 K. The small bulge at ~60 K might be due to AFM coupling within the Mn-rich layers. This feature is a probably a consequence of the complex competition between FM and AFM ordering mentioned above. The existence of AFM coupling is consistent with the small saturation moment (0.31 $\mu_B$ per Mn atom at 2 K).

The functional dependencies of the real, $\chi'$, (right y-axis) and imaginary, $\chi''$, (left y-axis) components of

![Figure 4](image)

Figure 4. (a) Real components of ac magnetization as a function of temperature in an applied field of $5/4\pi 10^3$ Am$^{-1}$ as a function of frequencies shown in top right corner; (b) Real (right y-axis) and imaginary components (left y-axis) of AC magnetization as a function of temperature from 3 to 35 K in an applied field of $5/4\pi 10^3$ Am$^{-1}$ as a function frequencies shown in top right corner. (c) ln $\tau$ vs. ln ($T''_f - T_{RCG}$)/$T_{RCG}$. (d) Time dependence of normalized magnetization at 2 K after cooling the sample in a field of 500/$4\pi 10^3$ Am$^{-1}$, removing the field and measuring the magnetization vs. time when the magnetic field reach zero. All measurements are performed on $x = 0.05$ samples.
Figure 5. (a) ZFC and FC hysteresis loops at 2 K. Inset shows enlarged view of the low field part. Exchange anisotropy and coercivity enhancements are evident; (b) Coercive field, $H_C$, and exchange bias field, $H_{EB}$, obtained from the hysteresis loops. The uncertainty should mainly come from remanence of the superconducting magnet which is smaller than the symbols’ size; (c) Reversed hysteresis loop obtained at 20 K. Arrows indicate the sweep direction. The arrows in the insets schematically indicate the magnetization reversal. (d) Normal hysteresis loop obtained at 10 K. All measurements were performed on $x = 0.05$ samples.

the AC susceptibility on frequency, in the 2–35 K temperature range, are shown in Figure 4(b). Both values are normalized by their maximum values.

The $\chi''$ shows a frequency-dependent maximum at around 10 K. Note that at 0.1 K, the temperature step used, when the results obtained between 8.5 and 10.5 K, were taken, was quite small. Said otherwise, the heating rate was particularly low.

Figure 4(c) plots the relaxation times, $\tau$, where $\tau$ equals to $1/2\pi f$, and $f$ the frequency of the applied field, versus $T_f$, where $T_f$ is the temperature at which $\chi''$ is a maximum, assuming, the following relationship:[21]

$$\frac{\tau}{\tau_0} = \left(\frac{T''_f - T_{RCG}}{T_{RCG}}\right)^{-z v}$$

is operative. First, we determined $T_g = 8.8 \pm 0.05$ K, which gives the best linear fit and then, from the linear fit of the results shown in Figure 4(c), the dynamical critical exponent, $z v$, was found to be $2.46 \pm 0.4$, and the spin flipping time, $\tau_0$ was $3.4 \pm 0.9 \times 10^{-7}$ s. This relatively large flipping time agrees well with other reentrant cluster glass system suggesting that the glassy nature is due to a cluster and not individual spins.[22] Figure 4(d) plots a typical relaxation curve at 2 K, of the magnetization, $M$ (normalized by $M_o$, the magnetization at $t = 0$ when the magnetic field is removed) after FC in a magnetic field of 500/4$\pi \times 10^3$ Am$^{-1}$. All these features are consistent with a cluster glass state at $T < 10$ K.

Based on these results, it is reasonable to assume that upon cooling, some of the Mn atoms, residing on the Cr sites, form Mn-rich regions in a Mn-poor matrix (Figure 3(d)). The former undergoes a paramagnetic to FM transition at a $T_c$ that depends on the Mn concentration in that region. The Mn-poor matrix, on the other hand, undergoes a reentrant cluster glass transition at $\sim 30$ K.

For all temperatures studied, and regardless of whether the sample was ZFC or FC, $M$ did not saturate (e.g. Figure 5(a)), indicating the presence of an AFM interaction, in accordance with our interpretation above.

To study the exchange coupling, the DC magnetization was measured at different temperatures after cooling from 350 K in either ZFC or FC mode. The corresponding hysteresis loops at 2 K are shown in Figure 5(a). The 2 K FC M-H loop exhibits a negative shift, whereas the ZFC M-H loop shows no shift (see inset in Figure 5(a)). The exchange bias field, $H_{EB}$ and coercive fields, $H_C$ obtained from the hysteresis
loops, at various temperatures, are shown in Figure 5(b). Exchange anisotropy usually emerges as a result of coupling between FM–AFM, FM–FI or, as the case here, FM-spin glass states at the interface.[23] According to the above phase transition interpretation, it is reasonable to conclude that coupling between the Mn-rich, FM regions and the reentrant cluster glass Mn-poor matrix gives rise to the exchange anisotropy. As discussed below, from 10 to 30 K, the exchange bias field, $H_{EB}$, decreases greatly.

At 20 K, $H_{C}$ is negative since the hysteresis loops are inverted (Figure 5(c)). Inverted hysteresis loops are rare in nature. Not coincidentally, they have been observed in exchange coupled multilayers.[24–26] Such inverted loops are a consequence of the interplay of magnetization reversal and magneto-crystalline anisotropy.[24] In other words, it is reasonable to assume that the interplay between Mn-rich regions and the reentrant cluster matrix is responsible for the inverted loops. The magnetization reversal mechanism is shown schematically in the insets shown in Figure 5(c); those for the normal hysteresis loop in the insets shown in Figure 5(d). For the 20 K hysteresis loop, the Mn-poor regions (R regions) reverse their magnetization first at positive fields, followed by the Mn-rich regions (R regions) at negative fields. For the 10 K, normal hysteresis loop, the reversal mechanism is different. It follows that the different magnetization reversal sequences of the Mn-rich regions (R regions) and the Mn-poor regions (P regions) or matrix, give rise to the inverted loops at 20 K and normal hysteresis loops at 10 K.

Since the degree of inhomogeneity is tunable—as shown by our quenching experiment, for example—the exchange anisotropy, in turn, can also be readily tuned. Thus as elucidated herein, (Cr$_{1-x}$Mn$_x$)$_2$GeC can be synthesized to be a homogeneous [10] or an inhomogeneous complex system. Note that since the changes in the lattice parameters due to the incorporation of Mn in Cr$_2$GeC are negligible, the introduction of various interfaces can be carried out with little, to no, lattice mismatches.

To summarize, the plethora of magnetic phenomena observed in (Cr$_{1-x}$Mn$_x$)$_2$GeC can be viewed as a consequence of the competition between intralayer FM and interlayer AFM order.[10] The intricate competition between the two states could in principle be tuned by altering the interlayer distances. Considering the rich chemistry of the MAX phases, there will indubitably be more magnetic phases. If some of them happen to be M$_3$AX$_2$ or M$_4$AX$_3$, then the effect of varying the interlayer distances can be explored since the latter have larger c-lattice parameters than the M$_2$AX phase studied herein. The c-lattice parameters of the M$_2$AX, M$_3$AX$_2$ and M$_4$AX$_3$ are, respectively, of the order of 1.3, 1.8 and 2.3 nm.[1] Accordingly, the aforementioned competition may result in new equilibrium states.

In addition to the discovery of Mn$_2$GaC, two additional new exciting recent developments bode well for our ability to fine tune the FM–AFM competition. The first is the possibility of exfoliating the MAX phases themselves into nanosheets comprising a few MAX layers, which has been demonstrated in the Ti$_3$Si$_{1-x}$Al$_x$C$_2$ system.[27] The second is the complete etching of the A-layers from in between the MX layers phases to form a totally new class of 2D materials labeled MXenes.[28,29] In the latter, the coupling between layers is quite weak. Based on the analysis outlined herein, it is reasonable to assume that both types of exfoliated layers would yield a multitude of quite interesting magnetic responses and tunabilities.

In conclusion, the introduction of nanoscale inhomogeneities in bulk polycrystalline (Cr$_{1-x}$Mn$_x$)$_2$GeC samples, wherein Mn-rich layers are embedded within a Mn-poor matrix, gives rise to complex magnetic behavior. The Mn-rich layers are FM and the Mn-poor matrix undergoes a reentrant cluster glass transition at low temperatures. Due to the varying magnetic states of the Mn-poor region, the coupling between the two phases results in exchange anisotropy, and inverted hysteresis loops at 20 K. The tunable coupling of the layered magnetic (Cr$_{1-x}$Mn$_x$)$_2$GeC and other magnetic MAX phases may be of great potential in spintronic applications.

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