Evolution of magnetic properties in the normal spinel solid solution Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$

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Received 10 October 2011, in final form 3 December 2011
Published 6 January 2012
Online at stacks.iop.org/JPhysCM/24/046003

Abstract

We examine the evolution of magnetic properties in the normal spinel oxides Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ using magnetization and heat capacity measurements. The end-member compounds of the solid solution series have been studied in some detail because of their very interesting magnetic behavior. MgCr$_2$O$_4$ is a highly frustrated system that undergoes a first-order structural transition at its antiferromagnetic ordering temperature. CuCr$_2$O$_4$ is tetragonal at room temperature as a result of Jahn–Teller active tetrahedral Cu$^{2+}$ and undergoes a magnetic transition at 135 K. Substitution of magnetic cations for diamagnetic Mg$^{2+}$ on the tetrahedral A site in the compositional series Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ dramatically affects magnetic behavior. In the composition range 0 $\leq$ x $\leq$ $\approx$ 0.3, the compounds are antiferromagnetic. A sharp peak observed at 12.5 K in the heat capacity of MgCr$_2$O$_4$ corresponding to a magnetically driven first-order structural transition is suppressed even for small x. Uncompensated magnetism—with open magnetization loops—develops for samples in the x range $\approx$0.43 $\leq$ x $\leq$ 1. Multiple magnetic ordering temperatures and large coercive fields emerge in the intermediate composition range 0.43 $\leq$ x $\leq$ 0.47. The Néel temperature increases with increasing x across the series while the value of the Curie–Weiss $\theta_{CW}$ decreases. A magnetic temperature–composition phase diagram of the solid solution series is presented.

(Some figures may appear in colour only in the online journal)

1. Introduction

Materials with the spinel structure display a wide range of functional properties and are applied as battery electrodes [1], multiferroic materials [2, 3] and catalytic materials [4]. In addition, spinels offer unique opportunities for the exploration of exotic magnetic phenomena [5–7]. A rich diversity of possible magnetic ground states can be found in materials with the spinel structure. These range from long range ordered ferrimagnetic states, observed in magnetite Fe$_3$O$_4$, to degenerate spin liquid states seen in systems with geometrically frustrated interactions such as ZnCr$_2$O$_4$ [8]. In spinels with the general formula AB$_2$O$_4$, cation A and B sites can both be occupied by magnetic ions. Coupling between the various magnetic ions gives rise to a number of competing exchange pathways and a multitude of possible ground states. Additional complexity arises when antiferromagnetically coupled cations populate the pyrochlore B sublattice in spinels. In this configuration, geometric constraints preclude the realization of a unique ground state resulting in frustrated systems. Slight perturbations of highly degenerate spin liquid states in frustrated magnets can result in a range of novel behaviors [9, 10].

Strongly frustrated three-dimensional pyrochlore B sublattices occur in oxide spinels with a non-magnetic A site and a chromium B site. Cr$^{3+}$ with a [Ar]3d$^3$ electron configuration shows a preference for the octahedral site where crystal field splitting stabilizes a half-filled 1$^2g$
level separated in energy from an empty $e_8$ level [11, 12]. Antiferromagnetic nearest-neighbor (NN) interactions between Cr$^{3+}$ ions populating the pyrochlore B sublattice cannot be fully satisfied. Pyrochlore sublattices with antiferromagnetically coupled spins have been shown to result in frustrated Heisenberg spin Hamiltonian expressions where NN interactions alone would not result in a single low energy state even at $T = 0$ K [13–16]. Given the strongly frustrated Cr$^{3+}$ sublattice, the choice of A site cation can profoundly affect magnetic properties in chromium oxide spinels.

Magnetic ground states depend strongly on the A cation in ACr$_2$O$_4$ spinels. Non-magnetic A site (for instance A = Zn, Mg, Cd) chromium oxide spinels are highly frustrated [17]. Spin–lattice coupling resolves the large ground state degeneracy by selecting a unique ordered state via a spin Jahn–Teller effect at the magnetic ordering temperature [16]. In magnetic A site spinels (for instance, A = Co, Fe, Cu, Mn), A–O–Cr coupling dominates over frustrated Cr–Cr interactions and non-collinear ferrimagnetic ground state are attained [3, 18–22]. Understanding changes in interactions due to the gradual addition of magnetic ions on the A site of frustrated ACr$_2$O$_4$ spinels is important. In this study, we investigate the magnetic properties of the solid solution Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ where the end members MgCr$_2$O$_4$ and CuCr$_2$O$_4$ differ both structurally and magnetically.

The canonical geometrically frustrated spinel MgCr$_2$O$_4$ crystallizes in the cubic space group $Fd\bar{3}m$ at 300 K. The pyrochlore Cr$^{3+}$ sublattice is based on a triangular motif where antiferromagnetic NN Cr–Cr coupling is geometrically frustrated. As a result, the spins in MgCr$_2$O$_4$ remain disordered far below the theoretical ordering temperature ($\Theta_{CW} \approx -400$ K) [23, 24]. A structural distortion lifts the spin state degeneracy of the pyrochlore Cr$^{3+}$ sublattice at the Néel temperature ($T_N$) $\approx 12.5$ K. The tetragonal space group $I4_1/amd$ has been suggested as the low symmetry crystallographic structure [25, 26]. A sharp peak in heat capacity coincident with the magnetically driven structural transition in MgCr$_2$O$_4$ denotes the first-order nature of this transition [27].

The spinel CuCr$_2$O$_4$ is cubic above 873 K [28, 29], with Cu$^{2+}$ occupying tetrahedral sites and Cr$^{3+}$ populating octahedral sites. In the cubic phase, tetrahedral crystal field splitting of the $d^9$ Cu$^{2+}$ energy level results in triply degenerate high lying $t_2$ subshells and fully occupied low energy $e_8$ subshells [30]. Distortion of the CuO$_4$ tetrahedra lifts the orbital degeneracy of the $t_2$ level, and when these distortions are coherent, the symmetry of CuCr$_2$O$_4$ is lowered from cubic $Fd\bar{3}m$ to tetragonal $I4_1/amd$ [31]. Magnetic studies of CuCr$_2$O$_4$ show that it is ferrimagnetic at 135 K. The magnetic structure in the ordered state is triangular with Cr$^{3+}$ in the 001 planes aligned parallel but at an angle to Cr$^{3+}$ in adjacent planes. Cu$^{2+}$ align antiparallel to the net moment of the Cr$^{3+}$ sublattices forming a magnetic structure comprising triangles of spins [19].

Previous work has investigated the local and average structural changes in the series Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ [32]. These studies show that, although local distortions occur for all Cu$^{2+}$-substituted compositions, cooperative structural changes are dependent on $x$ and on temperature. For example, at room temperature, compounds of the series Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ remain cubic on average for $x < 0.43$. Tetragonal average symmetry driven by cooperative Cu$^{2+}$ Jahn–Teller distortions appears in compositions with $x > 0.43$ at 300 K.

We study the effect of introducing magnetic, Jahn–Teller active Cu$^{2+}$ on the non-magnetic A site of Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ on magnetic frustration and on the nature of magnetic interactions. A previous study of the Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ system showed that addition of Co$^{2+}$ on the non-magnetic Zn$^{2+}$ site quenched frustration across the series [33]. Here, we explore changes in magnetic behavior as Jahn–Teller active tetrahedral Cu$^{2+}$ induces lattice distortions in addition to adding magnetism on the A site of the Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ compounds [32]. Novel properties such as intrinsic exchange bias have been shown to exist at phase boundaries [34]. We therefore closely examine the region between the antiferromagnetic and ferrimagnetic phases in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ for unusual phenomena.

2. Experimental details

Polycrystalline samples of the series Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ ($x = 0, 0.1, 0.2, 0.43, 0.47, 0.6, 0.8$ and 1) were prepared through calcination of nitrate precursors as reported by Shoemaker and Seshadri [32]. The samples were structurally characterized by laboratory x-ray diffraction using a Philips X’pert diffractometer with Cu Kα radiation. Phase purity was confirmed in selected compositions using high-resolution synchrotron powder x-ray diffraction collected at the 11-BM beamline at the Advanced Photon Source. Some of the samples have also been previously characterized by time-of-flight neutron scattering which verified that all the spinels are normal, meaning the B site is purely Cr$^{3+}$, and there is no Cr$^{3+}$ on the A site. Magnetic susceptibility measurements on powder samples were performed using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. In all samples, magnetization as a function of temperature was measured at a field of 0.1 T. Isothermal field-dependent magnetization measurements were performed at 2 and 5 K. A Quantum Design physical properties measurement system was used to measure heat capacity at 0 T for various temperature ranges selected to accommodate the magnetic transition temperature of each sample. For the heat capacity measurements, pellets of 50% sample mass and 50% silver mass were prepared by grinding and pressing at about 330 MPa. Silver was used to increase mechanical strength and thermal conductivity. The pellets were mounted on the sample stage using Apiezon N grease. The heat capacity of the grease and of silver were collected separately and subtracted to obtain the sample heat capacity.

3. Results and discussion

We study the magnetic properties of the compounds Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ using magnetic susceptibility measurements. Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility collected under a DC field of 1000 Oe
in the temperature range 300 K

Calculated spin-only values of

magnetization at low temperatures increase with $x$

samples $x > 0.5$. Magnetic ordering temperatures and the

magnetization at low temperatures increase with $x$ concentration.

Alternative data points are omitted to enhance clarity.

**Table 1.** Magnetic data of the series Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$.

Experimental $\mu_{\text{eff}}$ and $\Theta_{\text{CW}}$ obtained from fitting susceptibility data in the temperature range 300 K $\leq T \leq$ 390 K to the Curie–Weiss equation. $T_N$ is taken as the temperature where $d\chi/dT$ is maximum. Calculated spin-only values of $\mu_{\text{eff}}$ are also presented.

| $x$  | $\mu_{\text{eff}}$ ($\mu_B$, exp.) | $\mu_{\text{eff}}$ ($\mu_B$, calc.) | $\Theta_{\text{CW}}$ (K) | $T_N$ |
|------|-----------------------------------|-----------------------------------|--------------------------|-------|
| MgCr$_2$O$_4$ | 5.42 | 5.47 | $-368$ | 12.5 |
| $x = 0.1$ | 5.34 | 5.50 | $-361$ | 10.5 |
| $x = 0.2$ | 5.24 | 5.53 | $-329$ | 16 |
| $x = 0.43$ | 5.17 | 5.59 | $-314$ | 37.27 |
| $x = 0.47$ | 4.94 | 5.60 | $-295$ | 38.29 |
| $x = 0.6$ | 4.89 | 5.64 | $-262$ | 35 |
| $x = 0.8$ | 4.54 | 5.69 | $-202$ | 91 |
| CuCr$_2$O$_4$ | 4.48 | 5.74 | $-148$ | 128 |

as a function of temperature shows a composition-dependent ordering temperature ($T_N$) defined as the temperature where $d\chi/dT$ is maximum (figure 1 and table 1). $T_N$ increases with Cu$^{2+}$ substitution. In addition to Cr$^{3+}$–Cr$^{3+}$ interactions that are present in all compositions, Cu$^{2+}$–Cr$^{3+}$ and Cu$^{2+}$–Cu$^{2+}$ interactions occur in MgCr$_2$O$_4$ samples. The increase in $T_N$ correlates well with the increase in the number of magnetic interactions. It is also likely that Cu$^{2+}$ moments compensate some of the Cr$^{3+}$ sublattice moments. As Cr$^{3+}$ are compensated, the difficulty involved with satisfying antiferromagnetic interactions between spins on a pyrochlore lattice is alleviated, easing frustration and allowing magnetic order at high $T_N$. The $x = 0.1$ sample shows a lower $T_N$ indicating suppressed magnetic order for small amounts of magnetic ions on the non-magnetic A site of MgCr$_2$O$_4$. Concurrent structural and magnetic transitions occur in MgCr$_2$O$_4$ and structural studies of the compound $x = 0.1$ will enhance the understanding of the magnetic properties observed here. The decrease in $T_N$ with dilute doping of magnetic cations on the A site of a frustrated antiferromagnet has been observed in the system Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ [33].

In samples $x = 0, 0.1$ and 0.2 susceptibility increases to a maximum at $T_N$ before decreasing below $T_N$ (figure 1(c)). This trend in both ZFC and FC data indicates dominant antiferromagnetic interactions. A sharp cusp is observed at $T_N$ in MgCr$_2$O$_4$ where long range magnetic order occurs via a spin-driven Jahn–Teller transition [35]. This cusp broadens in samples $x = 0.1$ and 0.2, indicating changes in the magnetic ground state with Cu$^{2+}$ doping. The decrease in ZFC susceptibility coupled with the increase in FC susceptibility below $T_N$ in compositions $x = 0.43, 0.47, 0.6, 0.8$ and 1 (figures 1(a) and (b)) demonstrates ferrimagnetic behavior. The magnitude of the low temperature susceptibility increases with Cu$^{2+}$ content as shown in figure 1.

There are two ordering temperatures in the magnetic susceptibility of samples $x = 0.43$ and 0.47 (figure 2, table 1). This suggests the presence of two different kinds of long range interactions, coexisting long range order and a glassy state, or magnetic compensation. We find strong evidence for two distinct coexisting long range ordered states. Structural studies of these samples showed that compositions $x \leq 0.43$ have a cubic average structure at room temperature. Under similar conditions, compositions $x \geq 0.47$ showed tetragonal average symmetry. Average cubic and tetragonal symmetry was present in the range $0.43 \leq x \leq 0.47$ at 300 K. Shoemaker and Seshadri suggest that, although locally CuO$_4$ tetrahedra are distorted for Cu$^{2+}$ content $<0.43$ due to the Jahn–Teller activity of tetrahedral Cu$^{2+}$, the average structure remains cubic at 300 K. At $x = 0.43$, the distorted CuO$_4$ distribution is sufficient to cause a cooperative effect and the tetragonal phase appears [32]. Here, magnetic susceptibility studies complement structural studies well. We find that, in Cu$^{2+}$ concentrations $x \leq 0.2$, magnetism
is antiferromagnetic as occurs in MgCrO$_4$. For $x$ above 0.6, ferrimagnetism develops (figure 1). Although addition of Cu$^{2+}$ increases the degree of non-compensation of B site spins, the B–B interaction dominates at low $x$ values. Multiple transitions at $x = 0.43$ suggest that A–O–B coupling is sufficient to cause ferrimagnetic (Fi) long range order in addition to antiferromagnetic (AF) order. We attribute the presence of two magnetic transitions in the range $0.43 \leq x \leq 0.47$ to coexisting Fi and AF interactions. Evidence of structural phase separation in the range $0.43 \leq x \leq 0.47$ at 300 K supports the magnetic data showing two distinct, yet coexisting, kinds of magnetic order [32]. For $x > 0.6$, ferrimagnetism prevails. We probe the sample $x = 0.43$ for glassy behavior that may alternatively cause one of the two transitions observed in this sample.

Random interactions in a spin glass result in highly irreversible dynamic magnetization states well probed by ac susceptibility measurements. A common signature of glassy behavior is a frequency-dependent magnetic transition temperature. Figure 3 shows frequency-dependent susceptibility measurements of the compounds Mg$_{0.57}$Cu$_{0.43}$Cr$_2$O$_4$ (a) and Mg$_{0.6}$Cu$_{0.4}$Cr$_2$O$_4$ (b). The sharp cusp at $T_N$ associated with the antiferromagnetic transition of highly frustrated systems appears at all measured frequencies for Mg$_{0.57}$Cu$_{0.43}$Cr$_2$O$_4$. In Mg$_{0.57}$Cu$_{0.43}$Cr$_2$O$_4$ a broad transition appears for all probed frequencies. The two well-resolved magnetic transitions of Mg$_{0.57}$Cu$_{0.43}$Cr$_2$O$_4$ measured during dc zero-field-cooling (figure 2(b)) are present in the ac measurement but they are much poorly resolved. The frequency independence of the magnetic transitions in both compounds shows small amounts of disorder in these samples. These measurements provide further evidence for coexisting ferrimagnetic and antiferromagnetic regions in the mixed composition compounds.

**Figure 3.** Magnetic ac susceptibility of the compounds (a) Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and (b) Mg$_{0.57}$Cu$_{0.43}$Cr$_2$O$_4$ taken with an ac field of 1 Oe under zero dc field. The magnetic ordering temperature of both compounds is frequency-independent. We highlight approximate magnetic ordering temperatures.

High temperature susceptibility data was fitted to the Curie–Weiss (CW) equation (equation (1)) to obtain the effective paramagnetic moment ($\mu_{eff}$) and $\Theta_{CW}$:

$$\chi = \frac{C}{T - \Theta_{CW}}.$$  

(1)

The Curie constant ($C$) yields an effective paramagnetic moment following the expression $\mu_{eff} = \sqrt{3k_B C/\gamma_N}$. $\Theta_{CW}$ is a measure of the strength and nature of magnetic interactions. A plot of the scaled normalized inverse susceptibility shown by equation (2) simplifies comparison of magnetic behavior in compounds where magnetic interactions evolve significantly with composition [33]:

$$\frac{C}{\chi |\Theta_{CW}|} + \text{sgn}(\Theta_{CW}) = \frac{T}{|\Theta_{CW}|}.$$  

(2)

Inverse susceptibility scaled according to equation (2) using values obtained from Curie–Weiss fits of the high temperature susceptibility data 300 K $\leq T \leq 390$ K are presented in figure 4. Ideal CW paramagnetism occurs in all samples when $T/|\Theta_{CW}| \geq 1.5$ with the exception of CuCr$_2$O$_4$. In the paramagnetic regime, spins are disordered. Deviations from CW behavior denote the onset of long or short range interactions. Uncompensated interactions contribute to negative deviations, while compensated interactions lead to positive deviations. Compensated interactions in MgCr$_2$O$_4$ gradually become uncompensated with Cu$^{2+}$ doping. On the
basis of powder neutron diffraction, Prince [19] has proposed the magnetic structure of CuCr$_2$O$_4$ to consist of triangular ordering, where Cr$^{3+}$ sublattices in (001) sheets are parallel within each plane but at an angle to Cr$^{3+}$ moments on other planes. The net moment from the Cr$^{3+}$ sublattice is partially compensated by the Cu$^{2+}$ sublattice. It is likely that this effect, which increases the number of uncompensated interactions, develops gradually with Cu$^{2+}$ substitution in MgCr$_2$O$_4$. Negative deviations from ideal CW behavior in CuCr$_2$O$_4$ when $T/|\Theta_{CW}| \geq 1$ indicate the presence of strong range uncompensated interactions above $T_N$ (figure 4).

The normalized CW plot is a direct indicator of frustrated magnetism. $T_N/|\Theta_{CW}|$ is the inverse of the frustration parameter ($f$). The onset of long range order when $T/|\Theta_{CW}| \ll 1$ is a sign of strong frustration [36]. The canonical geometrically frustrated antiferromagnet, MgCr$_2$O$_4$, shows a high frustration index (figure 4, table 1). Surprisingly, the compound $x = 0.1$ is the most frustrated of the series despite the presence of random Cu$^{2+}$ ions. The increase in frustration index despite the addition of small amounts of magnetic ions on the non-magnetic A site of geometrically frustrated systems has been shown in the study of Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ by Melot et al. [33]. Magneto-structural studies of the compound Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ will likely shed light onto the enhanced frustration index. Except for the composition $x = 0.1$, Cu$^{2+}$ doping eases frustration in MgCr$_2$O$_4$ and this occurs because of the disruption of symmetric Cr$^{3+}$-Cr$^{3+}$ interactions with random Cu$^{2+}$ distribution in the doped compounds. Cu$^{2+}$ interferes with $B$-$B$ coupling by adding Cu$^{2+}$-Cr$^{3+}$ and Cu$^{2+}$-Cu$^{2+}$ interactions. Additionally, crystal distortions arise in Cr$_4$O$_6$ due to the Jahn–Teller effect of Cu$^{2+}$, depending on proximity to CuO$_4$ tetrahedra. Differences in Cr–Cr distances and Cr–O–Cr angles due to structural distortions break the degeneracy of exchange coupling routes, ultimately easing frustration.

Values obtained from fitting high temperature susceptibility data to the CW equation are presented in table 1 and plotted in figure 5. An expected spin-only effective moment for series compositions is calculated using the expression

$$\mu_{\text{eff}} = \sqrt{\mu_C^2 + 2\mu_C^2}. $$

The moment of each magnetic cation (c) is calculated using the equation $\mu_c = g_S(S+1)\mu_B$, in which $g$ is the Landé $g$ factor and has the approximate value 2. $S = 1/2$ and $3/2$ when $c$ is Cu$^{2+}$ and Cr$^{3+}$ respectively. The effective moment is expected to increase with Cu$^{2+}$ concentration. Surprisingly, a decrease in $\mu_{\text{eff}}$ occurs with Cu$^{2+}$ doping. We speculate that short range interactions develop in the paramagnetic regime in Cu$^{2+}$-rich samples leading to the underestimation of the spin-only effective moment. Curie–Weiss fitting at temperature $\geq 390$ K may yield $\mu_{\text{eff}}$ values that are closer to what is expected. The underestimation of $\mu_{\text{eff}}$ with increased substitution of magnetic ions on the A site of a frustrated magnetic system has been reported in the system Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ [37]. The orbital contribution to the effective magnetic moment in octahedral Cr$^{3+}$ and Jahn–Teller active Cu$^{2+}$ is expected to be heavily quenched; hence, the orbital moment is not considered.

A negative theoretical ordering temperature ($\Theta_{CW}$) is determined for all samples, confirming that spin coupling results in antiferromagnetic or ferrimagnetic order. The magnitude of $\Theta_{CW}$ decreases with Cu$^{2+}$ content. A similar trend in Curie–Weiss temperature has been reported in the systems Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ [37] and Cd$_{1-x}$Cu$_x$Cr$_2$O$_4$ [38]. These earlier works postulate that the decrease is due to interactions from the Cu$^{2+}$ sublattice. Strong B–B interactions in MgCr$_2$O$_4$ yield the largest $|\Theta_{CW}|$ value measured. Possibly, the addition of magnetic Cu$^{2+}$ on the diamagnetic A site of MgCr$_2$O$_4$ disrupts the B–B interaction contributing to weaker interactions in Cu$^{2+}$-doped samples. The increase in $T_N$ with Cu$^{2+}$ concentration coupled with the decrease in the theoretical ordering temperature ($\Theta_{CW}$) results in a dramatic decrease of the frustration parameter with Cu$^{2+}$ content. In agreement with previous similar studies [33, 37, 38], we find that frustration is strongly quenched with the addition of spins in the A sublattice. These results show that lattice geometry does not prevent spin order in Cu$^{2+}$-doped samples. The sample $x = 0.1$ exhibits a curious trend. In this compound, the frustration index increases despite Cu$^{2+}$ doping. This was also observed in the study of magnetism of the series Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ [33].

Entropy changes are well described by specific heat measurements. A sharp peak in the specific heat of MgCr$_2$O$_4$ indicates changes in entropy at $T \approx 12.5$ K (figure 6(a)). The transition temperature recorded in heat capacity coincides with the magnetic ordering temperature, signaling the onset of long range AF order. A broad shallow peak at $T \approx 11$ K appears at the magnetic ordering temperature of the sample $x = 0.1$, suggesting that there is a remanent magnetic entropy below the ordering temperature (figure 6(b)). In the sample Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$, there is no anomaly in the specific heat at the magnetic ordering temperature while for the sample
Mg$_{0.57}$Cu$_{0.43}$Cr$_2$O$_4$, a broad hump develops at 30 K $\leq$ $T$ $\leq$ 70 K (figure 6(d)). The absence of any entropy changes after the onset of magnetic order suggests the presence of glassy spin states. However, we find no evidence of this is the ac susceptibility measurements (figure 3). It is likely that non-collinear magnetic ordered states with finite entropy appear in Cu-doped samples explaining the absence of any anomalies in the specific heat for these compositions.

A progressive transition from antiferromagnetic to ferrimagnetic order is observed in isothermal field-dependent magnetization measurements (figure 7). In MgCr$_2$O$_4$, a linear dependence of the magnetization on the field that is characteristic of antiferromagnetic order is observed. Slight nonlinearity in the field-dependent magnetization develops at $\pm$1.5 T in MgCr$_2$O$_4$ (figure 7(a)). This nonlinearity originates from a field-driven change in local magnetic structure as postulated by Suzuki et al [23]. Antiferromagnetism persists in samples $x$ = 0.1 and 0.2 (figures 7(b), (c)). However, coercivity develops as the loops are open upon close examination. Coercivity is highest in samples $x$ = 0.43 and 0.47 (figures 7(d), (e)). Additionally, earlier studies on exchange bias effects in these compounds revealed an increase in the exchange bias field ($H_E$) with Cu$_{2+}$ in samples $x$ = 0.1, 0.2 and 0.43 [32]. Antiferromagnetic–ferrimagnetic interfaces are a common cause of enhanced coercivity and shifted hysteresis [39, 40]. Given that the samples $x$ = 0.43 and 0.47 bridge the AF and Fi regions, we propose that pinning of spins at the Fi–AF cluster interfaces contributes to the enhanced coercivity.

Coupled with the increased coercivity in compounds $x$ = 0.43 and 0.47 is the change from AF to Fi behavior that is evident in field- and temperature-dependent behavior. In samples with $x$ = 0.6, 0.8 and 1, the coercivity decreases and the field-dependent magnetization becomes ferrimagnetic. CuCr$_2$O$_4$ has a coercive field ($H_C$) of about 0.25 T and a saturation moment of 0.68 $\mu_B$ per formula unit. The Néel model of antiferromagnetism predicts a saturation moment of 5 $\mu_B$ per formula unit in CuCr$_2$O$_4$. Since the predicted moment far exceeds the measured value, neutron diffraction measurements in the ordered state were used to resolve this discrepancy [19]. According to the magnetic structure proposed by Prince, the triangular arrangement of spins explains the low moment. Cr$_{3+}$ on the 001 planes are aligned parallel and opposite to Cr$_{3+}$ in adjacent planes yielding a net moment from the Cr$_{3+}$ sublattices. The Cu$_{2+}$ sublattice couples antiferromagnetically to the net moment of the Cr$_{3+}$ sublattices creating a triangular configuration of spins. A composition-dependent saturation magnetization is observed in samples $x$ = 0.43, 0.47, 0.6, 0.8 and 1. The saturation moment increases with Cu$_{2+}$.

We can assemble the (Mg, Cu)Cr$_2$O$_4$ magnetic phase diagram in figure 8 by combining magnetic ordering transitions and heat capacity measurements for the various compositions in this study. Transition temperatures specified

Figure 6. Temperature-dependent heat capacity of compounds with $x$ = 0, 0.1, 0.2 and 0.43 in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ under zero field. (a) Heat capacity of the sample $x$ = 0 showing a sharp peak at 12.5 K; (b) a broader peak occurs at 11.5 K in the sample $x$ = 0.1; (c) in the samples with $x$ = 0.2, a smooth decrease in heat capacity with temperature is observed and (d) the sample with $x$ = 0.43 displays a broad bulge in the heat capacity at $\approx$50 K.

Figure 7. Isothermal magnetization traces of the different Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ compounds, measured at 2 K except for the samples with $x$ = 0.6 and 0.8 which were measured at 5 K. Compound (a) $x$ = 0 shows a linear variation of magnetization with field. Magnetic anisotropy induces slight nonlinearity at $\pm$1.5 T as reported by Suzuki et al [23]. In (b) $x$ = 0.1 and (c) $x$ = 0.2 linear dependence of the magnetization on field is again observed. In (d), the $x$ = 0.43 sample and in (e) the $x$ = 0.47 sample display a larger increase in magnetization as compared to samples with $x$ = 0.1 and 0.2. A large coercive field develops as observed from the wide hysteresis loops. At high fields the magnetization does not saturate. The samples with (f) $x$ = 0.6 and (g) 0.8 are ferrimagnetic with open hysteresis loops and almost saturating magnetization. (h) Field dependence of the magnetization of CuCr$_2$O$_4$ at 2 K showing well-behaved hysteresis and an almost saturated magnetization of 0.7 $\mu_B$ per formula unit with small coercive field.
by anomalies in susceptibility and heat capacity measurements are used to demarcate phase boundaries. MgCr$_2$O$_4$ enters a long range AF state at $T = 12.5$ K marked by sharp anomalies in both susceptibility and heat capacity. The sharp cusp in the susceptibility of MgCr$_2$O$_4$ is replaced with a rounded peak in compositions $x = 0.1$ and 0.2. The linear dependence of the magnetization on field as well as the temperature-dependent magnetization of samples $x = 0.1$ and 0.2 show that they are antiferromagnetic. In the range 0.2 $\leq x \leq 0.6$, coexisting ferrimagnetic and antiferromagnetic states exist as shown by large coercive fields and the absence of any glassy magnetism in selected compositions in this range studied using ac susceptibility. Mg$_{0.57}$Cu$_{0.43}$Cr$_2$O$_4$ and Mg$_{0.53}$Cu$_{0.47}$Cr$_2$O$_4$ show two transition temperatures clearly indicated in the phase diagram. In the sample $x = 0.6$, ferrimagnetism develops indicated by the similarities in field- and temperature-dependent magnetization between the compound and the end-member CuCr$_2$O$_4$. All compositions are paramagnetic above the magnetic transition temperatures.

4. Conclusions

Recent years have seen renewed focus on frustrated magnetic systems as a consequence of the recognition that they can give rise to exotic magnetic ground states [36, 41, 42]. The introduction of spins in the A site of geometrically frustrated spinels has been suggested as a means of relieving frustration [33, 37, 38]. We find, in agreement with this proposition, that Cu$^{2+}$ alleviates frustration in all Mg$_{2-x}$Cu$_x$Cr$_2$O$_4$ compositions studied with the exception of $x = 0.1$. Temperature- and field-dependent magnetization indicate a largely antiferromagnetic ground state in the compositions $x < 0.2$, coexisting ferrimagnetic and antiferromagnetic states with open hysteresis loops in the range $0.2 \leq x \leq 0.6$, and largely ferrimagnetic ground states for $x > 0.6$, albeit with significantly smaller saturation magnetization than would be found for Néel-ordered states. Specific heat measurements support these conclusions for samples with small $x$. Emergent behavior at the AF/Fi phase boundary, indicated by large coercive fields and multiple magnetic transition temperatures, suggests microscopic interactions between AF and Fi clusters.

Acknowledgments

MCK thanks Joshua Kurzman and Phillip Barton for helpful comments. We gratefully acknowledge support from the National Science Foundation through a Materials World Network grant (DMR 0909180). MCK is supported by the Schlumberger Foundation Faculty for the Future Fellowship. SLM is supported by the RISE program at the Materials Research Laboratory. Use of shared experimental facilities of the Materials Research Laboratory: an NSF MRSEC, supported by NSF DMR 1121053 is acknowledged. The MRL is a member of the NSF-supported Materials Research Facilities Network (www.mrfn.org). The 11-BM beamline at the Advanced Photon Source is supported by the Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC02-06CH11357.

References

[1] Thackeray M M, de Picciotto L A, de Kock A, Johnson P J, Nicholas V A and Adendorff K T 1986 J. Power Sources 21 1
[2] Yamasaki Y, Miyasaka S, Kaneko Y, He J-P, Arima T and Tokura Y 2006 Phys. Rev. Lett. 96 207204
[3] Lawes G, Melot B, Page K, Ederer C, Hayward M A, Proffen Th and Seshadri R 2006 Phys. Rev. B 74 024413
[4] Zheludev V and Gao Q 2009 Microporous Mesoporous Mater. 124 144
[5] Yaresko A N 2008 Phys. Rev. B 77 115106
[6] Glazkov V N, Farutin A M, Tsurkan V, Krug von Nidda H-A and Loidl A 2009 Phys. Rev. B 79 021131
[7] Ueda H, Katori H A, Mitamura H, Goto T and Takagi H 2005 Phys. Rev. Lett. 94 047202
[8] Lee S-H, Broholm C, Ratcliff W, Gasparovic G, Huang Q, Kim T H and Cheong S-W 2002 Nature 418 856
[9] Balents L 2010 Nature 464 198
[10] Moessner R and Ramirez A P 2006 Phys. Today 59 24
[11] Dunitz J D and Orgel L E 1957 J. Phys. Chem. Solids 3 318
[12] Miller A 1959 J. Appl. Phys. 30 4
[13] Anderson P W 1956 Phys. Rev. 102 1008
[14] Lee S-H et al 2007 J. Phys.: Condens. Matter 19 145259
[15] Moessner R and Chalker J T 1998 Phys. Rev. Lett. 80 13
[16] Tchernyshyov O, Moessner R and Sandholt S L 2002 Phys. Rev. Lett. 88 067203
[17] Kant C, Deisenhofer J, Tsurkan V and Loidl A 2010 J. Phys.: Conf. Ser. 200 032032
[18] Ederer C and Komelj M 2007 Phys. Rev. B 76 064409
[19] Prince E 1957 Acta Crystallogr. 10 554
[20] Shirane G, Cox D E and Pickart S J 1964 J. Appl. Phys. 35 3
[21] Tomiyasu K, Fukunaga J and Suzuki H 2004 Phys. Rev. B 70 214434
[22] Bordacs S, Varjas D, Kezsmarki I, Mihaly G, Balassarre L, Abouelsayed A, Kuntscher C A, Ohtgushi K and Tokura Y 2009 Phys. Rev. Lett. 103 077205
[23] Suzuki H and Tsunoda Y 2007 J. Phys. Chem. Solids 68 2060
[24] Dutton S E, Huang Q, Tchernyshyov O, Broholm C L and Cava R J 2011 Phys. Rev. B 83 064407
[25] Ortega-San-Martin L, Williams A J, Gordon C D, Klemme S and Attfield J P 2008 J. Phys.: Condens. Matter 20 104238
[26] Ehrenberg H, Knapp M, Bahtz C and Klemme S 2002 Powder Diffract. 17 230
[27] Klemme S, O’Neill H S C, Schnelle W and Gmelin E 2000 Am. Mineral. 85 1686
[28] Kanamori J 1960 J. Appl. Phys. 31 S14
[29] Murthy K S R C, Ghose J and Rao E N 1983 J. Mater. Sci. Lett. 2 393
[30] Gerloch M 1981 Inorg. Chem. 20 638
[31] Dollase W A and O’Neill H S C 1997 Acta Crystallogr. C 53 657
[32] Shoemaker D P and Seshadri R 2010 Phys. Rev. B 82 214107
[33] Melot B C, Drewes J E, Seshadri R, Stoudenmire E M and Ramirez A P 2009 J. Phys.: Condens. Matter 21 216007
[34] Shoemaker D P, Rodriguez E E, Seshadri R, Abumohor I V and Proffen Th 2009 Phys. Rev. B 80 144422
[35] Lee S-H, Takagi H, Louca D, Matsuda M, Ji S, Ueda H, Ueda Y, Katsufuji T, Chung J-H, Park S, Cheong S-W and Broholm C 2010 J. Phys. Soc. Japan 79 011004
[36] Ramirez A P 1994 Annu. Rev. Mater. Sci. 24 453
[37] Yan L-Q, Macia F, Jiang Z-W, Shen J, He L-H and Wang F-W 2008 J. Phys.: Condens. Matter 20 255203
[38] Yan L-Q, Jiang Z-W, Peng X D, He L-H and Wang F-W 2007 Powder Diffract. 22 340
[39] Leighton C, Nogues J,Jonsson-Akerman B J and Schuller I K 2000 Phys. Rev. Lett. 84 3466
[40] Nogues J and Schuller K I 1999 J. Magn. Magn. Mater. 192 203
[41] Zhang Z, Louca D, Visinoiu A, Lee S-H, Thompson J D, Proffen Th, Llobet A, Qiu Y, Park S and Ueda Y 2006 Phys. Rev. B 74 014108
[42] Moessner R and Chalker J T 1998 Phys. Rev. B 58 12042