

X-Ray Absorption Spectroscopic and Magnetic Investigations on the Garnet $\text{Mn}_3\text{Al}_{2-x}\text{Cr}_x\text{Ge}_3\text{O}_{12}$

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Homogeneous garnet phases of the composition $\text{Mn}_3\text{Al}_{2-x}\text{Cr}_x\text{Ge}_3\text{O}_{12}$ were prepared through the decomposition of the corresponding metal acetates and oxalates at 1200°C. At temperatures below this, amorphous and/or partly crystalline intermediate stages were formed. Changes in the short-range order surrounding the metals during calcination were followed using XAS on the K-absorption edges of Ge, Mn, and Cr. The results indicate that at an annealing temperature of 730°C, Mn_3O_4 is formed as an intermediate compound. At temperatures of 1000°C and above, Mn(II) begins to occupy dodecahedron sites. At 295°C 37%, and at 335°C 30%, of chromium ions are present as tetrahedrally coordinated Cr(VI). The magnetic susceptibility of all quenched samples studied follows a Curie–Weiss law between 125 and 400 K. While $\text{Mn}_3\text{Cr}_2\text{Ge}_3\text{O}_{12}$ assumes ferrimagnetic ordering (with two Néel temperatures at 31 and 5.3 K) amorphous and partly crystalline intermediate compounds exhibit antiferromagnetism. The resultant zero-field cooled and field cooled susceptibilities split below the higher Néel temperature. These properties are indicative of a semi-spin-glass behavior. © 1995 Academic Press, Inc.

1. INTRODUCTION

The germanium garnets $\text{Mn}_3\text{Cr}_2\text{Ge}_3\text{O}_{12}$ and $\text{Mn}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$ were prepared as polycrystalline samples using the ceramic technique described by Tauber and Whinfrey (1). In using this technique it was found that it was not possible to use a stoichiometric amount of starting materials; a deficiency of the Ge component as well as an excess of Mn was required. It has been reported that among the germanium garnets, only $\text{Ca}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$ could be prepared using stoichiometric amounts of reactants (2). Our aim was to prepare $\text{Mn}_3\text{Al}_{2-x}\text{Cr}_x\text{Ge}_3\text{O}_{12}$ with $x = 0-2$ by means of a direct synthesis using stoichiometric amounts of initial materials (hereafter designed $3\text{Mn}/2 - x\text{Al}/x\text{Cr}/3\text{Ge}/y\text{O}$). Depending upon the annealing temperature, amorphous and partly crystalline intermediate compounds as well as the pure crystalline garnets were prepared.

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The short-range order surrounding the metals in the compounds during the crystallization was elucidated using XAS. This method yields information regarding geometry, valence, and bonding angles (XANES) as well as bond distances and the number of nearest neighbors (EXAFS) (3). Earlier investigations of other garnet systems showed that the short-range order in the amorphous precursors differs greatly from that in crystalline garnets (4, 5).

In these compounds the magnetic ions Mn(II) and Cr(III) are located on dodecahedral sites and octahedral sites, respectively. This arrangement gives rise to a magnetic exchange between ions that can lead to interesting magnetic properties. This was studied through susceptibility and magnetization measurements.

2. EXPERIMENTAL

The samples were prepared by thorough mixing of stoichiometric amounts of the following starting compounds: manganese (II) acetate tetrahydrate (Aldrich), aluminum (III) acetate hydroxide (Fluka), ammonium germanium (IV) oxalate tetrahydrate (Matthey), and chromium (III) acetate hydroxide (Aldrich). After being mixed, the substances were pressed into pellets. Subsequent annealing was performed at a heating rate of 200°C/hr. At temperatures ranging from 95 to 1200°C, samples were quenched at ambient room temperature and grain milled before further investigations were undertaken. For the investigation of thermal processes during the decomposition of the starting compounds, differential scanning calorimetry (DSC) in combination with thermogravimetry (TG) was employed (Netzsch STA 429 calorimeter). The decomposition is quite exothermic in air but not under argon (exothermic peak at 310°C). The mass decrease at temperatures up to 250°C is due to the evolution of NH_3 and H_2O , followed by a considerable weight loss at temperatures up to 350°C due to acetate/oxalate decomposition under CO and CO_2 formation.

The XAS measurements were performed using a double crystal monochromator at the EXAFS-II (Si (111))

and ROEMO-II (Si (311)) beamlines at the Hamburg Synchrotron Laboratory. In order to avoid sample inhomogeneities or undesirable absorption effects (6), the samples were prepared as pressed polyethylene pellets so that the product of the absorption coefficient μ and sample thickness d was approximately 2 ($\mu \times d \approx 2$). Standard EXAFS theory for data analysis was used (7).

The samples were also studied by X-ray diffraction. An increase in crystallinity with increasing annealing temperature was observed. The onset of garnet formation was found to occur at approximately 1000°C.

For magnetic measurements a SQUID susceptometer (Biomagnetic Technology Inc. VTS 905) was used. This equipment permits investigations encompassing a temperature range from 2 to 400 K and magnetic fields from 0 to 5 T.

3. RESULTS AND DISCUSSION

3.1. XAS Measurements on $Mn_3Cr_2Ge_3O_{12}$

XANES investigations on $Mn_3Cr_2Ge_3O_{12}$ were carried out on the Ge, Mn, and Cr *K*-edge and the resulting energy was calibrated; normalized spectra for the latter two edges are depicted in Figs. 1 and 2. The temperatures listed in the figures correspond to the maximal annealing temperatures.

The position of the Ge *K*-edge in the XANES spectra on the 3Mn/2Cr/3Ge/*y*O annealing series was determined to be independent of temperature. Comparison of the edge positions to those of standard compounds indi-

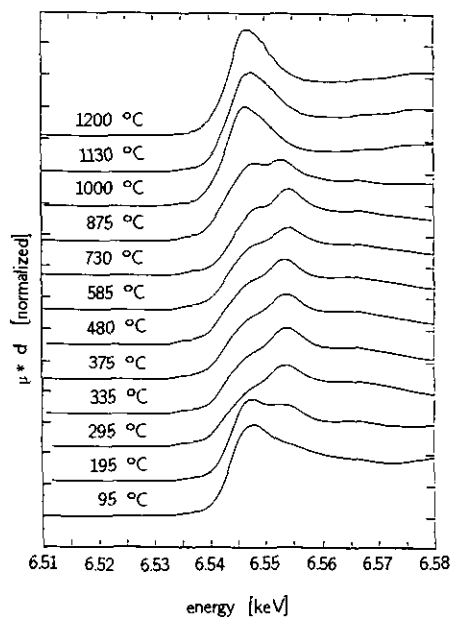


FIG. 1. Manganese *K*-edge XANES spectrum of the 3Mn/2Cr/3Ge/*y*O annealing series and of $Mn_3Cr_2Ge_3O_{12}$ (annealed at 1200°C).

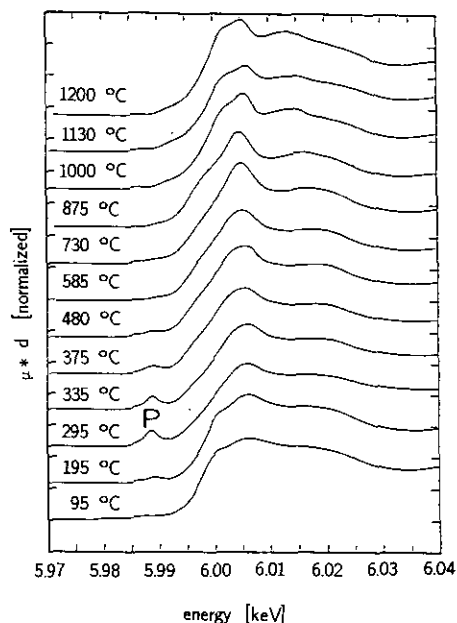


FIG. 2. Chromium *K*-edge XANES spectrum of the 3Mn/2Cr/3Ge/*y*O annealing series and of $Mn_3Cr_2Ge_3O_{12}$ (annealed at 1200°C).

cates that Ge has an oxidation number of IV throughout the entire temperature range. No changes in the XANES were observed for samples annealed at 1000°C and above. This reflects the fact that the garnet structure has already formed at these temperatures.

In Fig. 1 a striking shift is observed in the absorption maximum (from 6.547 to 6.553 keV) of the Mn *K*-edge spectra from samples annealed in the temperature range between 295 and 875°C. This shift is indicative of a partial oxidation of Mn(II) in the starting material to a mixed II/III oxidation state in an intermediate manganese oxide. Above 1000°C, Mn(II) structure is formed in the garnet following reduction of the mixed-valent intermediate.

The Cr *K*-edge XANES spectra of the 3Mn/2Cr/3Ge/*y*O series (Fig. 2) exhibit a preedge peak (P) at 5.988 keV with varying intensity at annealing temperatures between 195 and 480°C. This peak corresponds to a $1s \rightarrow 3d$ quadrupole transition and is an indication of the formation of tetrahedrally coordinated chromium (8, 9). Parallel to the development of this peak, partial oxidation of chromium (III) to chromium (VI) occurs. The amounts of tetrahedrally coordinated Cr(VI) and octahedrally coordinated Cr(III) present in the samples were estimated by fitting the XANES spectra through a linear combination of Cr *K*-edge XANES spectra of K_2CrO_4 (having tetrahedrally coordinated Cr(VI)) and Cr_2O_3 (with exclusively Cr(III) in octahedral coordination). The results of these fits are listed in Table 1. From Table 1 it is evident that the sample annealed at 295°C contains the largest amount of tetrahedrally coordinated chromium. Similar results for the

TABLE 1

Amounts of Octahedrally Coordinated Cr(III) and Tetrahedrally Coordinated Cr(VI) in the $3Mn/2Cr/3Ge/yO$ Annealing Series in the Lower Temperature Regime

Annealing temperature (°C)	O_h - Cr(III) (%)	T_d - Cr(VI) (%)
195	80	20
295	63	37
335	70	30
375	84	16
480	87	13

coordination of chromium during the crystallization process of $Gd_3CrGa_4O_{12}$ and $Gd_3Cr_2Ga_3O_{12}$ have been reported (10).

EXAFS investigations on $3Mn/2Cr/3Ge/yO$ were carried out at 10 K (Mn and Cr *K*-edges) and at room temperature (Ge *K*-edge). Using backscattering amplitudes and phases extracted from GeO_2 , MnO, and $YCrO_3$, the parameters N (coordination number) and R (interatomic distance) were determined by fitting the Fourier-filtered EXAFS oscillations from the first coordination sphere to the standard EXAFS equation. The first coordination shell of all metals was found to consist of oxygen nearest-neighbors, whereas the second shell results from a distribution of cation-cation distances and the next-nearest oxygen distance. In the case of germanium, these fits yielded $N = 4.3 \pm 1$ and $R = 1.74 \pm 0.02$ Å for samples which were annealed at $T = 875^\circ C$. This bond length is comparable to the average value found in the literature for GeO_2 of 1.739 Å (11). The average bond distance of the second coordination shell surrounding Ge exhibited an increase of ≈ 0.5 Å for samples annealed above $1000^\circ C$ compared to samples annealed at lower temperatures. This can be attributed to the onset of garnet formation.

The Fourier transforms of the Mn-K extended fine structure are depicted in Fig. 3. The lack of a second coordination shell peak in the modified radial distribution of the sample annealed at $95^\circ C$ is indicative of a large distribution of second shell distances such that they interfere destructively with one another. XRD results from samples annealed at $875^\circ C$ point to the manganese spinel Mn_3O_4 as one of the intermediate compounds formed during the crystallization process. The presence of Mn_3O_4 would also explain the formation of mixed valent Mn(II/III) elucidated in the XANES experiments. The Mn(III) ions in Mn_3O_4 are subject to Jahn-Teller distortions so that the first coordination sphere in this spinel is characterized by three bond lengths: one tetrahedral Mn-O distance and two Mn-O distances (equatorial and axial) for octahedra (12). Indeed, it was found that, for spectra obtained from $3Mn/2Cr/3Ge/yO$ samples an-

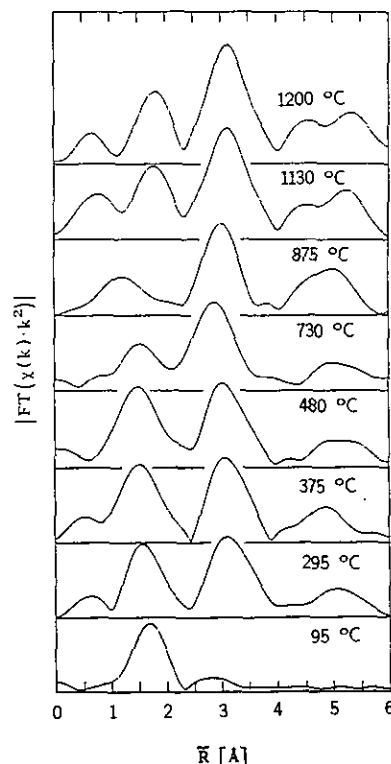


FIG. 3. k^2 -weighted Fourier transforms of the Mn *K*-edge EXAFS of the $3Mn/2Cr/3Ge/yO$ annealing series (Kaiser-Bessel window function, transformation range $3-11$ Å⁻¹).

nealed at 730 and $875^\circ C$, a three-shell fit of the backtransforms from the first manganese-oxygen coordination sphere leads to acceptable fit results. The structure parameters obtained from EXAFS fits listed in Table 2 show that in the annealing temperature range from 95 to $585^\circ C$ one Mn-O bond length exists, between 730 and $875^\circ C$ three Mn-O distances are present, due to the formation of a Mn_3O_4 intermediate, and above $1000^\circ C$ two different Mn-O bond lengths exist, resulting from a distorted dodecahedral Mn-O coordination in the garnet.

Similar to the Ge *K*-edge EXAFS results, the second peak in the Fourier transforms of the Cr *K*-edge EXAFS oscillations (Fig. 4) exhibits an increase in bond length of about 0.4 Å during the garnet formation. The coordination numbers and Cr-O bond distances obtained from one-shell fits of the backtransformed first shell data are listed in Table 2. For samples exhibiting preedge peak intensities (annealing temperatures between 195 and $480^\circ C$) an initial decrease in the mean coordination number of Cr followed by an increase in the number of oxygen nearest-neighbors was observed. These changes in N correspond well with the XANES results described above, where it was found that the mean Cr coordination number (as determined by the percent CrO_6 octahedra and CrO_4 tetrahedra elucidated from the fit procedure)

TABLE 2

Structural Parameters of the First Oxygen Coordination Shell of Manganese and Chromium in the $3\text{Mn}/2\text{Cr}/3\text{Ge}/y\text{O}$ Annealing Series

Annealing temperature (°C)	$N(\text{Mn})$	$R(\text{Mn})$ (Å)	$N(\text{Cr})$	$R(\text{Cr})$ (Å)
95	5.3	2.18	6.7	1.86
195	5.0	2.02	5.7	1.91
295	5.3	2.00	3.8	1.94
335	5.4	2.03	4.3	1.95
375	5.7	2.01	5.6	1.93
480	6.5	1.96	6.8	1.94
585	6.1	1.98	7.4	1.94
730	1.9	2.06	7.8	1.94
	3.9	1.96		
	4.0	2.36		
875	1.9	2.35	7.2	1.96
	3.9	2.00		
	3.9	2.12		
1000	4.2	2.25	6.7	1.92
	4.4	2.39		
1130	4.1	2.25	6.2	1.94
	4.2	2.38		
1200	4.0	2.26	6.2	1.91
	4.0	2.37		

Note. The values for N have an error of ± 10 – 20% , those for R of ± 0.02 Å.

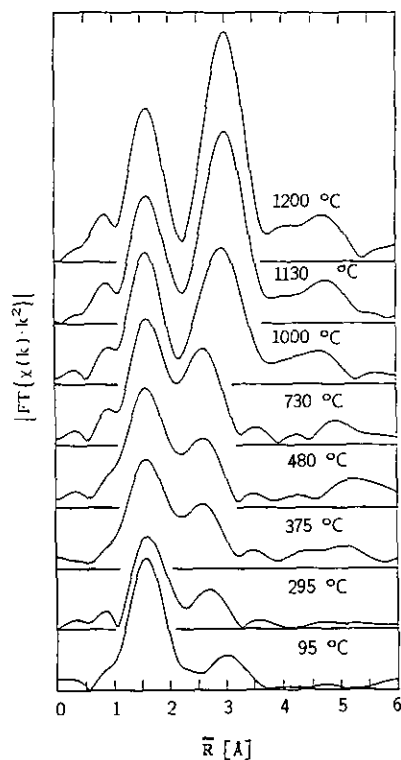


FIG. 4. k^2 -weighted Fourier transforms of the Cr K -edge EXAFS of the $3\text{Mn}/2\text{Cr}/3\text{Ge}/y\text{O}$ annealing series (Kaiser–Bessel window function, transformation range 3 – 11 Å $^{-1}$).

initially decreases and then increases within this same temperature range. Chromium ions occupy exclusively octahedral sites in samples annealed above 1000°C .

3.2. Magnetic Measurements on $\text{Mn}_3\text{Al}_{2-x}\text{Cr}_x\text{Ge}_4\text{O}_{12}$

Within the garnet structure, magnetic interactions may occur between adjacent Mn ions in dodecahedral sites via superexchange through O^{2-} ions. In contrast, Cr ions occupying octahedral sites are connected via exchange paths which include at least two O^{2-} ions (double exchange) (13). Antiferromagnetic ordering is observed in the case where only one of the three sublattices is occupied with magnetic ions, for example, in $\text{Mn}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$, where we determined $T_N = 6.3$ K. This value is comparable to earlier neutron scattering results, 7 K (14), and to results from heat capacity measurements, 6.65 K (15). In compounds where not only dodecahedral sites but also the octahedral sublattice is occupied with magnetic $3d$ ions, three interactions are effective: exchange within each of the two sublattices and one interaction between them. Upon increasing substitution of aluminum with chromium in the initially antiferromagnetic Mn–Al garnet, absolute values of paramagnetic Curie temperatures Θ_p decrease. This is indicative of increasing ferrimagnetic interactions.

Susceptibility measurements on $\text{Mn}_3\text{Al}_{2-x}\text{Cr}_x\text{Ge}_4\text{O}_{12}$ show that these compounds obey the Curie–Weiss law, whereby the best fit was obtained for temperatures in the range 140 – 360 K. The parameters derived from these measurements are listed in Table 3. The value of n_{eff} is due to 1 mole of magnetic ions and the value of n_{theo} is the mean calculated theoretical value for the magnetic ions on dodecahedral and octahedral sites (Mn(II) and Cr(III), respectively).

Between 2 and 10 K the course of the susceptibility with both zero-field cooling (ZFC) and field cooling (FC) was followed. To this end, the samples were initially cooled to 2 K in the absence of an external magnetic field; then a magnetic field was applied and susceptibility val-

TABLE 3

Paramagnetic Curie Temperatures Θ_p , Curie Constants C_{mole} , and the Experimental and Theoretical Number of Bohr Magneton n_{eff} and n_{theo} of $\text{Mn}_3\text{Al}_{2-x}\text{Cr}_x\text{Ge}_3\text{O}_{12}$

Molar Fraction x	Θ_p (K)	C_{mole} ($\times 10^{-4}$ m 3 K mole $^{-1}$)	n_{eff}	n_{theo}
2.0	4 (2)	2.01 (2)	5.06	5.10
0.5	1 (3)	1.89 (2)	5.17	5.23
1.0	–4 (1)	1.78 (2)	5.33	5.40
1.5	–12 (3)	1.68 (2)	5.53	5.62
0.0	–18 (2)	1.59 (4)	5.80	5.92

ues were recorded at temperatures up to 10 K (ZFC). Following this, χ values were again recorded while the temperature was decreased to 2 K (FC). From these results, two transition temperatures $T_{N1} = 3.1$ K and $T_{N2} = 5.3$ K (Fig. 5) were obtained. This is in accordance with results from other methods reported earlier (16, 17). The remarkable feature of our results is that the ZFC and FC susceptibilities take different courses, with FC susceptibility values being larger. It is known that such behavior can arise from partially frozen moments resulting in a certain spin glass character referred to as a semi-spin glass (18). Also evident is the fact that, due to diamagnetic exchange between Al and Cr ions, T_{N1} is less pronounced for compounds with larger amounts of aluminum.

The susceptibility of the $3\text{Mn}/2\text{Cr}/3\text{Ge}/y\text{O}$ series was also recorded as a function of annealing temperature (see Fig. 6). The paramagnetic Curie temperatures Θ_p listed in Fig. 6 were determined in the range 125–400 K. These values are negative for those samples annealed at temperatures below the onset of garnet formation. This is evidence for antiferromagnetic correlations with a Néel temperature of approximately 40 K. This behavior contrasts with that found in the crystalline garnet and may be attributed to ions occupying both octahedra and tetrahedra at lower annealing temperatures and also to the inhomogeneous nature of the samples, in that the intermedi-

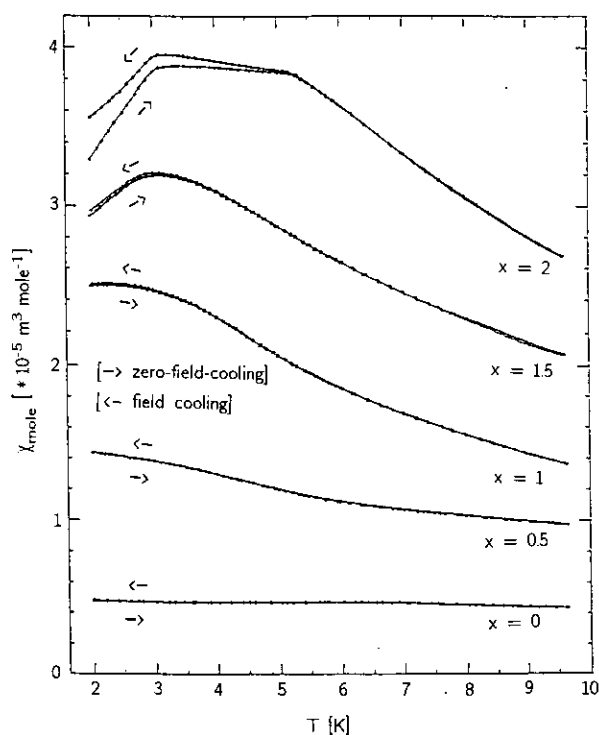


FIG. 5. Temperature dependence of the molar susceptibility of $\text{Mn}_3\text{Al}_{2-x}\text{Cr}_x\text{Ge}_3\text{O}_{12}$, measured in a magnetic field of 10 mT.

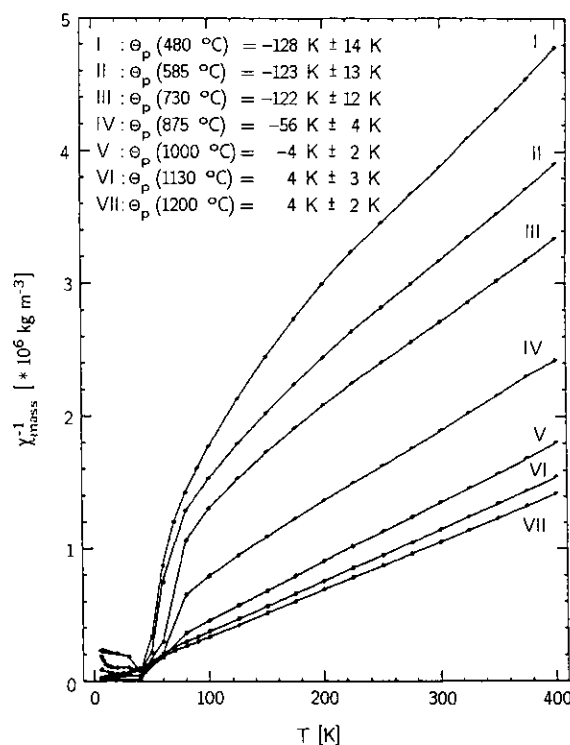


FIG. 6. Temperature dependence of the mass susceptibility of the $3\text{Mn}/2\text{Cr}/3\text{Ge}/y\text{O}$ annealing series. Θ_p denotes the paramagnetic Curie temperature (magnetic field: 100 mT).

ate Mn_3O_4 was found. At annealing temperatures above 1000°C , ferrimagnetic ordering with a Θ_p close to zero is established.

Magnetization measurements on $\text{Mn}_3\text{Al}_{2-x}\text{Cr}_x\text{Ge}_3\text{O}_{12}$ were carried out at 2 K. From these measurements it is evident that no saturation is achieved at magnetic fields up to 5 T for all garnet samples studied. Also, at 2 K, a slight isothermal remanence (ca. $1 \times 10^{-6} \text{ m}^3/\text{mole}$) was observed from $\text{Mn}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$.

4. CONCLUSION

Our magnetic investigations of $\text{Mn}_3\text{Al}_{2-x}\text{Cr}_x\text{Ge}_3\text{O}_{12}$ revealed that there is independent coupling of manganese and chromium ions in this compound. This results in two distinct Néel temperatures. Additional evidence is the decrease in the Néel temperature associated with chromium ions upon increasing dilution with aluminum. The resulting magnetic moment of the compounds gives rise to ferrimagnetic behavior. Furthermore, at low temperatures semi-spin-glass behavior is assumed.

Magnetic measurements on the calcination process of $3\text{Mn}/2\text{Cr}/3\text{Ge}/y\text{O}$ show that samples annealed at temperatures above 1000°C assume ferrimagnetic ordering. Samples quenched at temperatures below this exhibit antiferromagnetic behavior. XAS results indicate that the

magnetic ions in such quenched samples are distributed over octahedral and tetrahedral sites. Besides the existing sample inhomogeneities at low temperatures, this is probably the reason that the magnetic behavior of these samples deviates from that of the crystalline garnet.

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