THE INFLUENCE OF THE CO DOPING ON THE ELECTRONIC AND MAGNETIC PROPERTIES OF THE HALF-METALLIC FERRIMAGNET Mn_2VAl

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Abstract

Detailed investigations on the electronic and magnetic properties of the $Mn_{2-x}Co_xVAl$ (x = 0, 0.2, 0.6, 1.0) with ordered $L2_1$ structure have been performed. Polycrystalline samples have been examined by X-ray diffraction, magnetization measurements and valence band X-ray photoemission spectroscopy. The degrees of the B2 and $L2_1$ atomic ordering for the as-cast samples obtained from the intensity ratios of the X-ray patterns using Takamura's model , are higher than 0.80 and 0.52, respectively. The B2 ordering parameter increases over 0.94 for all the samples by thermic treatment (700-800º C, 72 h), while the $L2_1$ atomic ordering parameter shows only a modest increase. The Curie temperatures decrease with Co content, ranging between 757 K (x = 0) and 147 K (x= 1). Additionally, electronic band structure calculations using the Korringa-Kohn-Rostoker (KKR) Green's function method have been performed. The site occupation in the calculations has been correlated with those obtained by the X-ray diffraction, in order to account for the disorder effects. The measured valence band spectra are compared with those obtained by the KKR band structure method. As the Co doping is used to obtain a half-metallic fully compensated ferrimagnet (HMFi), our study may offer an insight on the evolution of the HMFi character with disorder and doping.

Experimental:

The $Mn_{2-x}Co_xVAl$ ingots were prepared by induction melting of the starting components under a purified Ar atmosphere and annealed at 700 and 800º C for 72 hours . The purity used as starting materials was Mn (99.95 wt%), Al (99.999 wt%), V (99.99 wt%) and Co (99.99 wt%). The crystal structure of the alloys was investigated at room temperature by using a Brüker D8 Advance diffractometer with Cu Kα radiation. Differential thermal analysis (DTA) was employed to study the structural transformations and phase transitions in the temperature range 100-1000º C under Ar atmosphere with a temperature ramp rate of 20º/min. Magnetization measurements were performed using an extraction magnetometer at the temperature of 2 K in applied external fields up to 10T. The Curie temperature were determined using the horizontal Weiss Balance magnetometer and the vibrating sample magnetometer (VSM).

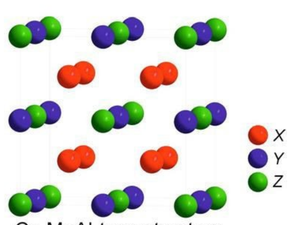
Theoretical details:

Calculations of the electronic band structure of the $Mn_{2-x}Co_xVAl$ compounds have been done in the framework of the Density Functional Theory using the spin polarized relativistic Korringa-Kohn-Rostoker (SPRKKR) method. The calculation method is based on the KKR-Green's function formalism that makes use of multiple scattering theory. The details of the calculation method have been described in details elsewhere [5]. The calculations have been done in the relativistic mode, i.e. all relativistic effects have been taken into account , including the spin-orbit coupling, in ferromagnetic and antiferromagnetic spin configurations. The angular momentum expansion of the basis functions was taken up to l = 2 for 3d metals and l = 1 for Al. Exchange and correlation effects have been treated within the framework of local spin density approximation (LSDA) using the GGA-PBE parametrization of Perdew et al.. The k-space integration was performed using the special points method . The substitutional disorder in the system has been accounted for by means of the Coherent Potential approximation (CPA) In order to ensure the correct band gap determination, the Lloyd formula has been employed.

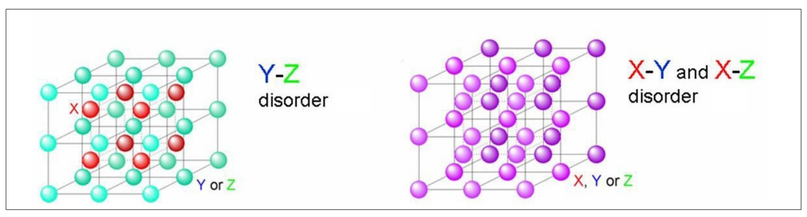
Results and Discussions:

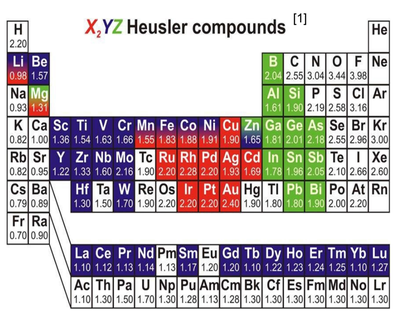
X_2YZ – space group
225 (F3_3m)
$L2_1$ or Cu_2MnAl-type

X (8c) (¼ ¼ ¼)
Y (4a) (0 0 0)
Z (4b) (½ ½ ½)



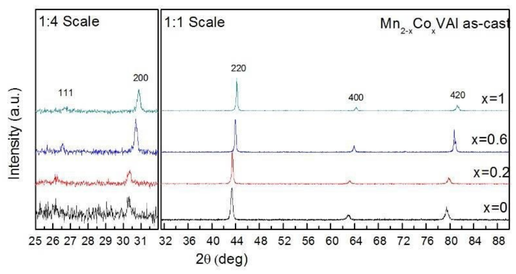
Cu_2MnAl-type structure (Heusler)



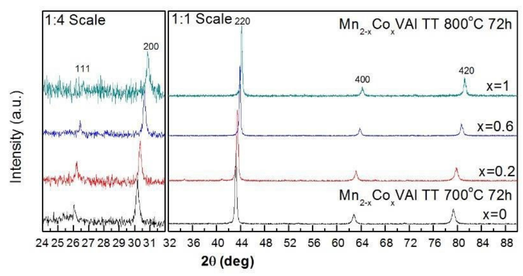


Structural and magnetic characterization

As-Cast

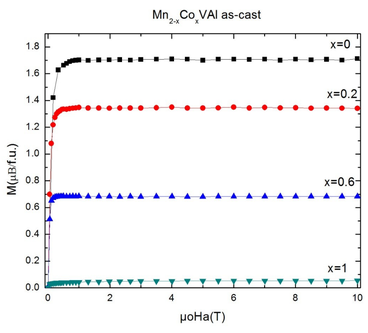


Annealed

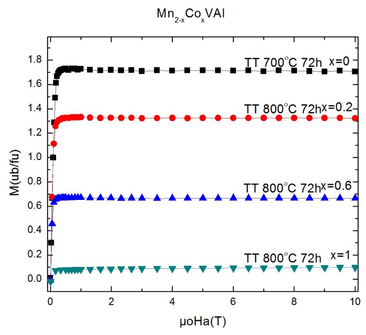


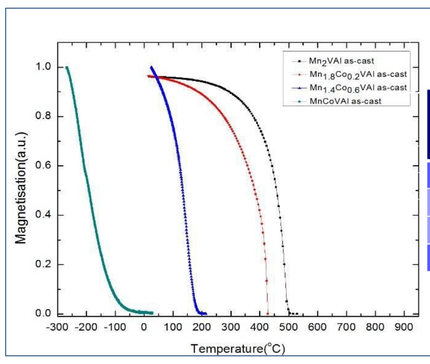
Co content (x)	Atoms	X site	Y site	Z site	S_{B2}	S_{L2}	a_{lat} (Å)
0	*Mn*	1.84	0.08	0.08	0.847	0.602	5.9087
	V	0.08	0.14	0.78			
	Al	0.08	0.78	0.14			
0.2	*Mn/Co*	1.96	0.02	0.02	0.953	0.684	5.8880
	V	0.02	0.84	0.14			
	Al	0.02	0.14	0.84			
0.6	*Mn/Co*	1.80	0.10	0.10	0.807	0.525	5.8533
	V	0.10	0.74	0.16			
	Al	0.10	0.16	0.74			
1.0	*Mn/Co*	1.86	0.07	0.07	0.855	0.521	5.8115
	V	0.07	0.75	0.18			
	Al	0.07	0.18	0.75			

Co content (x)	Atoms	X site	Y site	Z site	S_{B2}	S_{L2}	a_{lat} (Å)
0	*Mn*	1.99	0.005	0.005	0.9949	0.6616	5.8967
	V	0.005	0.83	0.165			
	Al	0.005	0.165	0.83			
0.2	*Mn/Co*	1.99	0.005	0.005	0.9974	0.7857	5.8765
	V	0.005	0.90	0.095			
	Al	0.005	0.095	0.90			
0.6	*Mn/Co*	1.99	0.005	0.005	0.9813	0.5899	5.8304
	V	0.005	0.79	0.205			
	Al	0.005	0.205	0.79			
1.0	*Mn/Co*	1.97	0.015	0.015	0.9386	0.9499	5.8003
	V	0.015	0.975	0.01			
	Al	0.015	0.01	0.975			

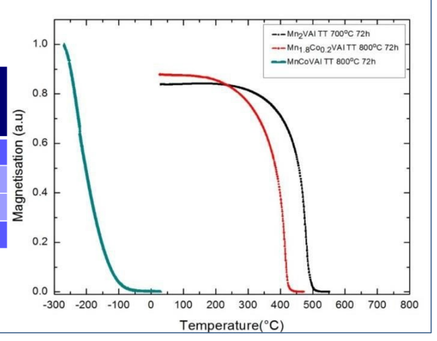


Content (x) $Mn_{2-x}Co_xVAl$	As-cast M_s (μB/f.u.)	Annealed M_s (μB/f.u.)	Other measurements
0	1.70802	1.71936	1.88 [3] 1.94 [4]
0.2	1.35031	1.32397	
0.6	0.68047	0.66526	
1	0.05098	0.08371	0.07 [3]

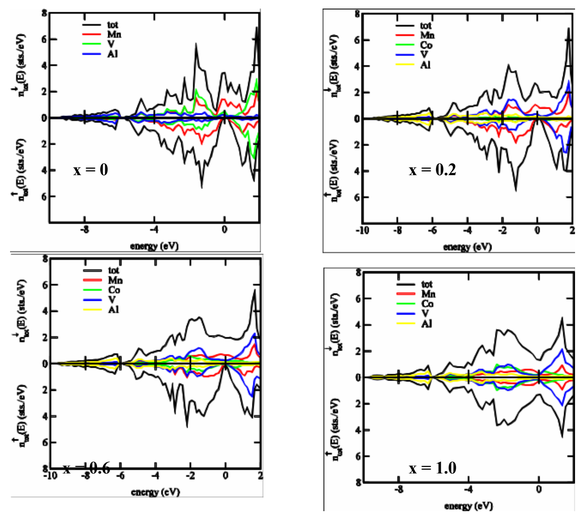




Content (x)	As-cast T_c (K)	Annealed T_c (K)	Other measurements T_c(K)
0	758	757	750 [3]
0.2	700	690	
0.6	433	-	
1	169	147	105 [3]



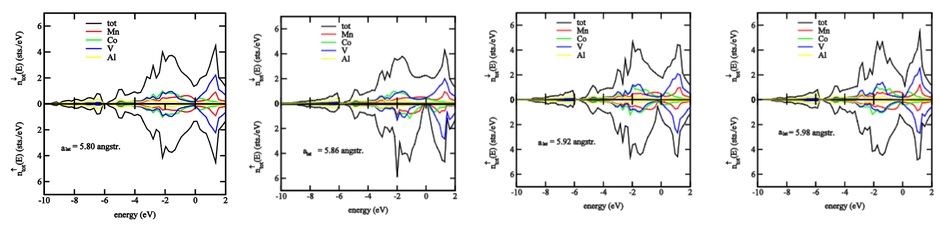
Band structure calculations for $Mn_{2-x}Co_xVAl$



	a_{lat}		Spin	Orbital
			m_s (μ_B)	m_l (μ_B)
X=0	5.89 Å	Mn 8c	1.58	0.03
		V 4a	-1.09	0.01
		Al 4b	-0.04	0.00
		Total	2.04	0.07
X=0.2	5.88 Å	Mn 8c	1.45	0.03
		Co 8c	-0.22	0.00
		V 4a	-0.92	0.01
		Al 4b	-0.03	0.00
		Total	1.63	0.05
X=0.6	5.83 Å	Mn 8c	1.07	0.01
		Co 8c	-0.14	0.00
		V 4a	-0.59	0.01
		Al 4b	-0.01	0.00
		Total	0.81	0.03
X=1.0	5.80 Å	Mn 8c	0.20	0.00
		Co 8c	-0.08	0.00
		V 4a	-0.10	0.00
		Al 4b	0.00	0.00
		Total	0.03	0.00

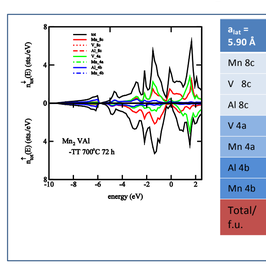
- *Experimentally determined lattice constants have been used*
- *The structure is 'ideal' (Mn/Co on 8c, V on 4a and Al on 4b site)*
- *Slater-Pauling rule: $m = N_{VAL} - 24$*

MnCoVAl : *evolution of the HMFi character with lattice constant*



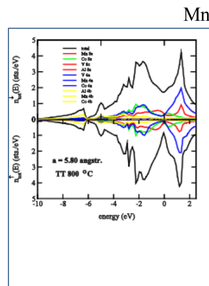
Disorder effects

Mn_2VAl



a_{lat} = 5.90 Å	Occupation	m_s (μ_B)	m_l (μ_B)
Mn 8c	0.98	1.58	0.03
V 8c	0.01	1.24	0.00
Al 8c	0.01	-0.08	0.00
V 4a	0.98	-1.07	0.01
Mn 4a	0.02	1.63	-0.02
Al 4b	0.98	-0.04	0.00
Mn 4b	0.02	-2.79	-0.01
Total/ f.u.		2.06	0.07

MnCoVAl



a_{lat} = 5.80 Å	Occupation	m_s (μ_B)	m_l (μ_B)
Mn 8c	0.48	0.32	0.00
Co 8c	0.48	-0.15	0.00
V 8c	0.02	0.42	0.00
Al 8c	0.02	-0.01	0.00
V 4a	0.98	-0.13	0.00
Mn 4a	0.01	-2.88	-0.01
Co 4a	0.01	-1.74	-0.12
Al 4b	0.98	0.00	0.00
Mn 4b	0.01	-2.85	-0.02
Co 4b	0.01	-1.83	-0.12
Total/f.u.		0.05	0.00

Site occupation used in the theoretical calculation is deduced from experimental XRD patterns

Mn_2VAl - $n^{\uparrow}$ band gap is narrowed by disorder;
- no major influence on the total magnetization
MnCoVAl - half-metallic character is absent

Magnetic exchange interactions (influenced by local symmetry and interatomic distances) → complex spin configuration

Conclusions and Perspectives:

$Mn_{2-x}Co_xVAl$

- All of the analyzed samples show **a fully ordered Heusler (X_2YZ) alloy with $L2_1$** structure at room temperature.
- Theoretical and experimental studies proves that the **degree of the B2 and $L2_1$ order increase by the appropriate heat treatment** (72 h at 700-800 °C).
- The saturation **magnetization values are slightly reduced** compared with those deduced from Slater-Pauling rule.
- **Curie temperatures decrease** by Co doping from 757 K for x=0 to 147 K for x=1.

MnCoVAl:

- The band structure calculations show the possibility to obtain a **half-metallic fully compensated ferrimagnet by expanding** the lattice constant.
- The Curie temperature near RT → **possible spintronic applications after further investigations**.

References:

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[2] Y. Takamura, R. Nakane, and S. Sugahara, J. Appl. Phys. **105**,109 (2009)
[3] B. Deka *et al.*, Journal of Alloys and Compounds **662**, 510 (2016)
[4] C. Jiang, M. Venkatesan, and J. M. D. Coey, Solid State Communications **118,** 513 (2001)
[5] Munich SPRKKR code, ebert.cup.uni-muenchen.de/**sprkkr**

Acknowledgment

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