

Quaternary Heusler Compounds without Inversion Symmetry: $\text{CoFe}_{1+x}\text{Ti}_{1-x}\text{Al}$ and $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$

Lubna Basit,^[a] Gerhard H. Fecher,^[a] Stanislav Chadov,^[a] Benjamin Balke,^{*[a]} and Claudia Felser^[a]

Dedicated to Professor John D. Corbett on the occasion of his 85th birthday

Keywords: Heusler compounds / Crystal structure / X-ray diffraction / Magnetic properties / Electronic structure

We report the quaternary Heusler compound derivatives $\text{CoFe}_{1+x}\text{Ti}_{1-x}\text{Al}$ and $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$, which do not have centers of inversion. Classical $\text{T}_2\text{T}'\text{M}$ (T, T' = transition metal, M = main group element) Heusler compounds (prototype: Cu_2MnAl) crystallize in the $L2_1$ structure, space group $Fm\bar{3}m$ (225) that exhibits a center of inversion. Replacing one of the T_2 atoms by another transition element (T'') results in a quaternary $\text{TT}'\text{T}''\text{M}$ compound with $F\bar{4}3m$ symmetry (Y; structure type LiMgPdSn) without center of inversion. In the case of "quasi closed shell" compounds with 24 valence electrons

in the primitive cell, one expects the absence of ferromagnetism according to the Slater–Pauling rule. Increasing the number of valence electrons will allow a study of the onset of the magnetic ground state. In this work, CoFeTiAl and iso-valent CoMnVAl as well as the accompanying solid solutions $\text{CoFe}_{1+x}\text{Ti}_{1-x}\text{Al}$ and $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$ were synthesized and their structure and magnetic properties investigated. $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$ ($x > 0$) is a half-metallic ferrimagnet in which the magnetic ground state is controlled by the strong localized moment at the Mn atoms replacing V.

Introduction

Heusler alloys or compounds are ternary intermetallics with a 2:1:1 stoichiometry.^[1,2] They first attracted interest when Heusler and coworkers^[1,3] showed that Cu_2MnAl is ferromagnetic, even though none of its constituents is ferromagnetic by itself. Interest in Heusler compounds persists as it has been established that their properties can be easily altered by replacement of elements. Co-based compounds have already been synthesized and investigated in the 1960s and 1970s.^[4,5] More recently they have attracted great interest, because they have been predicted to be half-metallic ferromagnets.^[6,7] Today Heusler compounds are used for various applications in spintronics,^[8] thermoelectrics,^[9,10] and superconductors.^[11] In this work, the properties of the solid solutions $\text{CoFe}_{1+x}\text{Ti}_{1-x}\text{Al}$ and $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$ have been investigated. It was expected that the partial replacement of Ti by additional Fe or V by additional Mn would keep the $F\bar{4}3m$ symmetry, but a transition from the Y to the X structure would be observed rather than to the $L2_1$ structure (Figure 1). The pure compounds ($x = 0$) carry 24 valence electrons in the primitive cell and are expected to exhibit no net magnetic moment. Therefore, the onset of

magnetic phenomena with increasing valence electron concentration can be studied by the degree of replacement. An advantage of these compounds is that the quaternary replacement used does not change the crystal symmetry globally or locally.

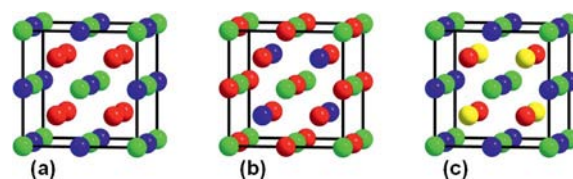


Figure 1. Crystal structure of the ternary $\text{T}_2\text{T}'\text{M}$ and quaternary $\text{TT}'\text{T}''\text{M}$ Heusler compounds. (a) $L2_1$ structure (Cu_2MnAl , $Fm\bar{3}m$, 225), (b) X structure (CuHg_2Ti , $F\bar{4}3m$, 216), (c) Y structure (LiMgPdSn , $F\bar{4}3m$, 216) (T = red, T' = blue, T'' = yellow, M = green).

Results and Discussion

Various types of ordered and disordered structures of Heusler compounds have been discussed by Bacon and Plant.^[13] The $L2_1$ structure^[14] of ternary Heusler compounds with 2:1:1 stoichiometry is a perfect 2^3 CsCl superstructure. The T_2 atoms form a primitive cubic sublattice, and adjacent cubes of this T_2 sublattice are alternately filled by T' or M atoms (Figure 1a). The primitive cell of the $L2_1$ structure contains four atoms that form the base of the fcc

[a] Johannes-Gutenberg-Universität, Institut für analytische und anorganische Chemie, 55099 Mainz, Germany
Fax: +49-6131-39-26267
E-mail: balke@uni-mainz.de

primitive cell. The result is a lattice with an $Fm\bar{3}m$ space group where the Wyckoff positions 4a (0,0,0), 4b (1/2,1/2,1/2), and 8c (1/4,1/4,1/4) are occupied by M, T', and T₂, respectively. The simple cubic sublattice is lost if one of the T₂ atoms is replaced by a third kind of transition metal, T''. At the same time, the symmetry is lowered to $F\bar{4}3m$, i.e. the center of inversion is lost. In this Y structure (termed for Heusler alloys in ref.^[13,15] as Y^a or Y_A) the Wyckoff positions 4a (0,0,0), 4b (1/2,1/2,1/2), 4c (1/4,1/4,1/4), and 4d (3/4,3/4,3/4) are occupied by M, T', T'', and T, respectively (Figure 1c).

The prototype for this structure is LiMgPdSn.^[16] Transforming the quaternary 1:1:1:1 compound back to a ternary structure but replacing T' by T keeps the $F\bar{4}3m$ symmetry without a center of inversion (Figure 1b). The result is that ternary TT'TM compounds with X structure (termed in ref.^[13,15] as X_a or X_A) are not equivalent to the T₂T'M compounds with $L2_1$ structure. The X structure type appears often for Heusler compounds when the ordinal number of T' is larger than that of T [$Z(T') > Z(T)$] and both are from the same period (for example 3d transition metals). It should be mentioned that all three structure types are converted to a simple bcc structure ($A2$, $Im\bar{3}m$) when all four positions are filled identically. This is the case for Heusler alloys with a random occupation of all lattice sites.

Figure 2 compares the XRD data of the two parent compounds CoFeTiAl and CoMnVAl. The typical fcc (111) and (200) reflections appear in the XRD pattern of both compounds. No impurities were detected by XRD. Refinement of the data reveals the lattice parameters $a_{\text{FeTi}} = 5.8509 \text{ \AA}$ for CoFeTiAl and $a_{\text{MnV}} = 5.8045 \text{ \AA}$ for CoMnVAl (300 K). The best R values were obtained for the Y structure [CoFeTiAl: $R_p(\text{Y}) = 6.6$, $R_{wp}(\text{Y}) = 8.7$; CoMnVAl: $R_p(\text{Y}) = 7.2$, $R_{wp}(\text{Y}) = 9.9$]. The difference between the measured and refined data shows some deviation at the (200) reflection that might be caused by a small amount of disorder. However, a fit for the X structure with intermixing of Fe and Ti or Mn and V has worthwhile results with R_p (R_{wp}) values being larger by 0.3 (1.0) for both compounds [CoFeTiAl: $R_p(\text{X}) = 6.9$, $R_{wp}(\text{X}) = 9.7$; CoMnVAl: $R_p(\text{X}) = 7.5$, $R_{wp}(\text{X}) = 10.9$]. Other types of disorder – swapping of Co–Ti, Co–V, or any intermixing of Al with one of the transition metals – lead to much higher R values and can be excluded. Only Co–Fe or Co–Mn interchange, or a slight deficiency of Al results in R values similar to or slightly lower than the pure Y structure. However, it is not possible to distinguish between these two types of disorder or the correct amount of disorder from measurements at single photon energy. The reason for this is that the number of parameters for the fit becomes larger than the number of distinguishable reflections.

Figure 3 compares the XRD data of the two solid solutions CoFe_{1+x}Ti_{1-x}Al and CoMn_{1+x}V_{1-x}Al. The typical fcc (111) and (200) reflections are small as already observed for the parent compounds. However, they are clearly resolved in most of the samples. The (111) reflection is absent in CoFe_{1.5}Ti_{0.5}Al, which is explained by *anti-site* disorder. As for the parent compounds, the particular type of disorder

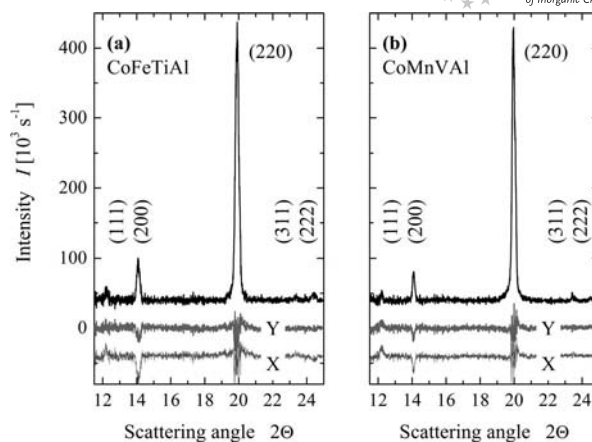


Figure 2. XRD data of CoFeTiAl (a) and CoMnVAl (b). The data were measured with Mo- K_α radiation. X and Y assign the difference between the data and the refinement as described in the text.

cannot be determined from these measurements with a conventional laboratory X-ray source. The lattice parameter found in the Rietveld refinement is unchanged within the error of the measurement. This indicates that the lattice parameter is dominated by the Co–Fe and Co–Mn sublattice interaction rather than interaction between the transition metal and main group element.

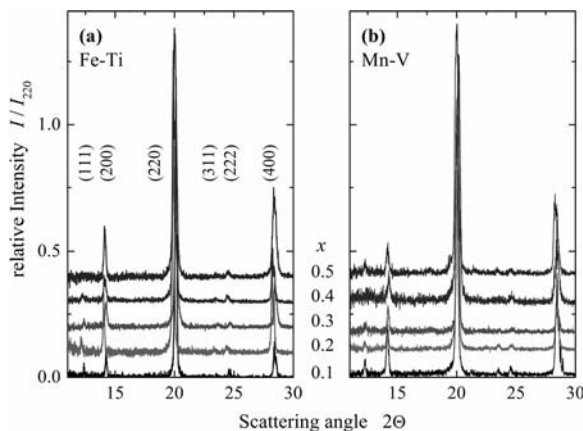


Figure 3. XRD data of CoFe_{1+x}Ti_{1-x}Al (a) and CoMn_{1+x}V_{1-x}Al (b). The data were measured with Mo- K_α radiation and normalized to the intensity of the (220) reflection. Data for $x > 0.1$ are plotted and offset for better comparison.

The magnetic moment (m) of many Heusler compounds, especially the Co₂-based half-metallic ferromagnets,^[8,17] follows the Slater–Pauling rule where there is an average magnetic moment (in multiples of the Bohr magneton, μ_B) per atom for localized moment systems according to Equation (1).

$$m_{\text{av}} = n_{\text{av}} - 6 - 2n_{\text{sp}} \quad (1)$$

n_{av} is the mean number of valence electrons per atom in an alloy or compound and n_{sp} arises from the average number of unbalanced minority sp electrons. The constant 6 arises from the fact that the d electrons are constrained

such that the Fermi energy falls into a minimum (or gap) between occupied and unoccupied d states and therefore minimizes the total energy.

In half-metallic ferromagnets with a gap in one of the spin densities or in quasi closed shell compounds all sp electrons are occupied, and the n_{sp} term vanishes. In 2:1:1 or 1:1:1:1 Heusler compounds there are four atoms in the primitive cell, and thus an overall magnetic moment results according to Equation (2).

$$m = (N_v - 24) \mu_B \quad (2)$$

N_v is the accumulated number of valence electrons in the primitive cell.^[17–20] Here there is $2 + n(d)$ for each transition metal and $2 + n(p)$ for the main group element, where the constant 2 arises in both cases from the s electrons, and $n(d)$ and $n(p)$ are the numbers of available d and p valence electrons, respectively. At $N_v = 24$ the materials are not ferromagnetic according to the Slater–Pauling rule. The reason is that a quasi closed shell character is reached at $N_v = 24$ caused by successive filling of the $a1$ (two s electrons), $t2$ (six p electrons), and e and $t2$ (together ten d electrons) bands, followed by subsequent complete filling of an additional $t2$ band (six d electrons). Deviations from Equation (2) appear when the compound is not in a half-metallic state and unbalanced sp or d electrons are present. For some of the $L2_1$ ordered compounds, 24 valence electrons lead to the phenomenon of half-metallic completely compensated ferrimagnetism^[21] in which the moments are ordered in a way that the total magnetic moment vanishes, even though individual magnetic moments have – other than in antiferromagnets – a different magnitude.^[22]

The magnetic data of the two solid solution series $\text{CoFe}_{1+x}\text{Ti}_{1-x}\text{Al}$ and $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$ are compared in Figure 4. Inset (c) in Figure 4(b) shows the hysteresis of $\text{CoMn}_{1.05}\text{V}_{0.95}\text{Al}$ measured at 300 K. This demonstrates that the Curie temperature is already above room temperature at the lowest Mn substitution of 5%. Similar to this composition, all samples of both series exhibited for $x > 0.05$ a ferromagnetic type hysteresis at 300 K. The shape of the hysteresis was soft magnetic in all cases. From the Slater–Pauling rule one expects that the saturation magnetization (sm) increases with the concentration x and the difference in the number of valence electrons given by Equation (3).

$$sm(x) = (\Delta N_v \times x) \mu_B \quad (3)$$

The differences ΔN_v are $4 e^-$ for the FeTi and $2 e^-$ for the MnV compounds. This results in magnetic moments of $2 \mu_B$ or $1 \mu_B$ at $x = 0.5$. The linear increase with increasing number of valence electrons is seen in Figure 4 for both series of compounds. The observed deviations – the higher values in the TiFe compounds at large x – are caused by *anti-site* disorder in the samples. Such disorder is often observed in Al-containing Heusler compounds. The low hybridization strength between Al and the surrounding transition metal atoms easily allows swapping between Al and the transition metal atoms.

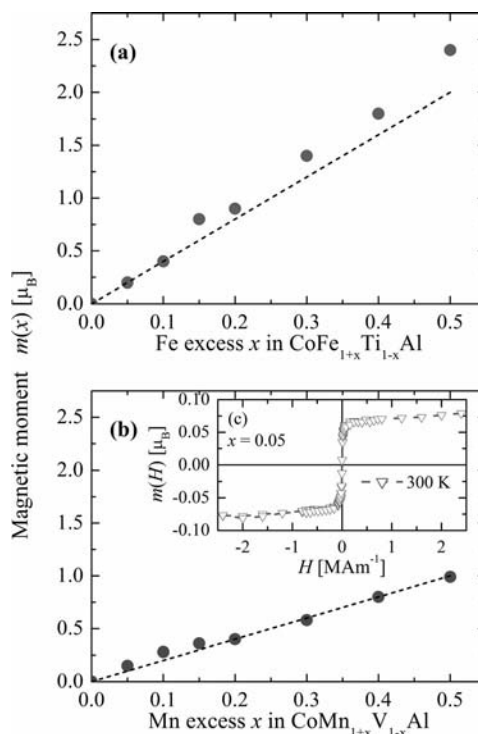


Figure 4. Magnetisation data of $\text{CoT}'_{1+x}\text{T}''_{1-x}\text{Al}$. The concentration dependence of the saturation magnetic moments of $\text{CoFe}_{1+x}\text{Ti}_{1-x}\text{Al}$ in (a) and of $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$ in (b) are shown. The measurements were performed at 5 K. The dashed lines correspond to the expected values from the Slater–Pauling rule. Inset (c) shows the hysteresis of $\text{CoMn}_{1.05}\text{V}_{0.95}\text{Al}$ measured at 300 K.

An increase in nearest neighbor transition metals leads to an enhancement of the magnetic moment, in particular for compounds containing Co and Fe. From the better agreement of the magnetization of $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$ with the Slater–Pauling values, it is expected that this series is a good candidate for half-metallic ferromagnetism.

The electronic structure of $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$ is analyzed in more detail because of its better structural stability. The absence of a magnetic moment in the parent compounds is already expected from the Slater–Pauling rule [Equation (2)]. On the other hand, one might expect the occurrence of half-metallic completely compensated ferrimagnetism.^[21] In particular for CoMnVAl a localized magnetic moment may appear at the Mn atoms and force a magnetic order. These experiments did not give any information on the magnetic order in the parent compounds; indeed, this may be caused by the fact that the magnetic transition takes place at a temperature far below 5 K. Therefore, *ab initio* calculations of the electronic structure were performed in order to determine the electronic ground state. *Ab initio* calculations of the electronic structure resulted in a non-spin-polarized ground state for the parent compounds. This result was obtained independently of the method used and starting parameters (ferromagnetic or different types of ferrimagnetic order). Therefore, half-metallic completely compensated ferrimagnetism can be excluded as the ground state. Going to the substituted alloy $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$, the

electronic structure turned into a ferrimagnetic ground state with increasing magnetic moments as observed in the experiment.

Figure 5 compares the electronic structure of pure CoMnVAl and its derivative CoMn_{1.5}V_{0.5}Al with increased Mn content. The density of states of the parent CoMnVAl is not spin-polarized, whereas it is split into majority and minority states in CoMn_{1.5}V_{0.5}Al. CoMnVAl exhibits a deep minimum at the Fermi energy. This minimum is closed in the majority states of CoMn_{1.5}V_{0.5}Al and open in the minority states at the same time. The result is an electronic structure typical for half-metallic ferromagnets. The total magnetic moment of CoMn_{1.5}V_{0.5}Al is 1 μ_B in agreement with the experiment. The magnetic order is ferrimagnetic with site-resolved magnetic moments of $m_{\text{Co}} \approx 0.40 \mu_B$, $m_{\text{MnA}} \approx -1.08 \mu_B$, $m_{\text{MnB}} \approx 2.97 \mu_B$, and $m_V \approx 0.45 \mu_B$.

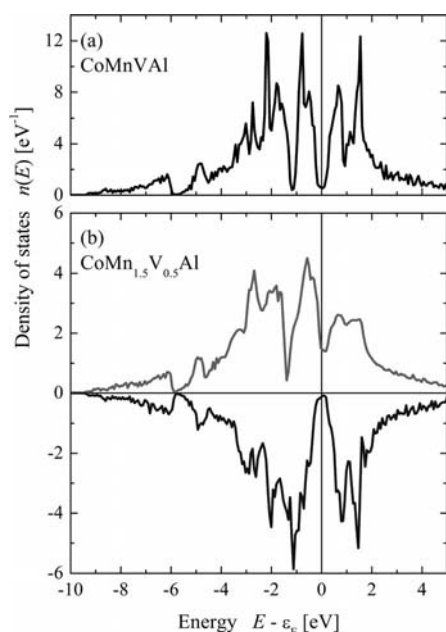


Figure 5. Electronic structure of CoMn_{1+x}V_{1-x}Al. The density of states of CoMnVAl is shown in (a) and that of CoMn_{1.5}V_{0.5}Al in (b).

Figure 6 shows the calculated magnetic moments for the solid solution series CoMn_{1+x}V_{1-x}Al. Only the spin moments are shown, because the influence of the orbital moments was negligible as found in fully relativistic calculations. The total magnetic moment follows Equation (3) and thus the expectation from the Slater–Pauling rule for half-metallic ferromagnets, which is in perfect agreement with the experiment. The absolute values of the moments in the primitive cell (Figure 6a) increase with increasing Mn content $1+x$ for Co and both types of Mn atoms. The strongest increase is observed at the Mn^B site that partially substitutes V. This increase is compensated by the negative moment at the Mn^A site, which results in the ferrimagnetic order. The magnetic moment at the V site exhibits a maximum at $x \approx 0.4$ demonstrating that the V content $1-x$ decreases slightly faster than the magnetic moment at the V atom increases.

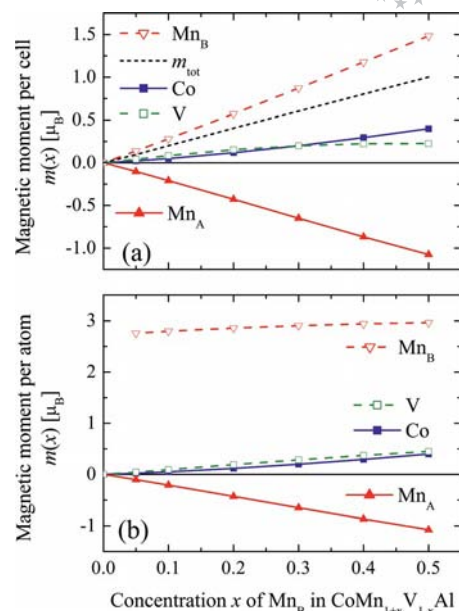


Figure 6. Calculated spin magnetic moments of CoMn_{1+x}V_{1-x}Al. The concentration dependence of the magnetic moments is shown, (a) gives the total and site-resolved moments in the primitive cell and (b) gives the site-resolved moments per atom.

More insight into the evolution of the magnetic state is found by comparing the concentration dependence of the magnetic moments at the individual atoms. Both atoms with fixed concentration (Co and Mn^A) as well as the V atoms exhibit a linear increase of the absolute moments with increasing concentration of Mn. The behavior of the Mn^B atoms is different. At a concentration of 5%, a localized magnetic moment of nearly 3 μ_B is obtained that increases slightly with increasing concentration. From this observation it is clear that the magnetism is formed by the Mn^B atoms. The magnetic moments at the remaining atoms simply increase with the growing influence of the Mn^B atoms. Pinning the Fermi energy in the gap of the minority states forces their magnetic moments to adopt values such that the total magnetic moment fulfills the Slater–Pauling rule.

Conclusions

The quaternary Heusler compounds CoFe_{1+x}Ti_{1-x}Al and CoMn_{1+x}V_{1-x}Al, which have no inversion symmetry, were synthesized and analyzed by XRD and magnetometry. Analysis of the electronic structure was based on ab initio calculations. The parent compounds ($x = 0$) crystallize in the Y structure with $F\bar{4}3m$ symmetry due to the 24 valence electrons in the primitive cell that do not carry magnetic moments either in the primitive cell or at the individual sites. This is remarkable for CoFeTiAl, because CoFe is the transition metal alloy that carries the largest magnetic moment and exhibits the highest known Curie temperature, and for CoMnVAl because Mn carries a localized magnetic

moment in all other Heusler compounds. The electronic structure calculations also reveal that the parent compounds do not show magnetic order, in agreement with the experiments.

With increasing substitution of Ti by Fe or V by Mn a linear increase of the magnetic moment with the number of valence electrons is observed that agrees with the Slater–Pauling rule, in both experiment and calculations. This demonstrates that the Slater–Pauling behavior of Heusler compounds is not restricted to the $L2_1$ structure with $Fm\bar{3}m$ symmetry but is also valid for $F\bar{4}3m$ symmetry.

The detailed analysis of the electronic structure of the solid solution series $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$ reveals a half-metallic ferrimagnetic ground state with a narrow band gap in the minority states for $x > 0$. At 5% concentration, a magnetic moment of about $3 \mu_B$ appears at the Mn^B atoms that partially replace V. Over the complete series, the magnetic order and moments at the remaining atoms are completely controlled by the strong localized moment at the Mn^B atoms.

Experimental Section

Polycrystalline ingots of the $\text{CoFe}_{1+x}\text{Ti}_{1-x}\text{Al}$ and $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$ series of compounds (with $0 \leq x < 0.5$, $x = 0.1$) were prepared by arc melting of stoichiometric amounts of high purity elements in an argon atmosphere. The resulting ingots were melted several times and turned over between melts to yield homogeneous samples. The weight of the ingots was monitored between the melting steps, and the loss of material was less than 1% after the last melting step. Finally, parts of the polycrystalline samples were annealed at 1300 K in evacuated quartz tubes for 15 d. The crystallographic structures were investigated by X-ray powder diffraction using $\text{Mo-}K_\alpha$ radiation (Bruker, AXS D8). The magnetic properties were investigated by means of a superconducting quantum interference device (SQUID, Quantum Design MPMS XL-5) at temperatures from 5 K to 300 K. The electronic structure calculations were performed by the fully relativistic spin-polarized KKR method with coherent potential approximation (CPA) for disordered systems.^[12] The CPA calculations for $\text{CoMn}_{1+x}\text{V}_{1-x}\text{Al}$ were performed in the $F\bar{4}3m$ space group with the following site occupations: Co on 4a, Mn^A on 4b, $x \text{ Mn}^B$ and $1 - x \text{ V}$ simultaneously on 4c, and Al on 4d.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (DFG) (research unit FOR559, projects P01 and P07) is gratefully acknowledged.

- [1] F. Heusler, *Verh. Dtsch. Phys. Ges.* **1903**, 5, 219.
- [2] O. Heusler, *Ann. Phys.* **1934**, 155, 411.
- [3] F. Heusler, W. Starck, E. Haupt, *Verh. Dtsch. Phys. Ges.* **1903**, 5, 220.
- [4] V. Y. Markiv, E. I. Hladyshevskii, Y. B. Kuzma, *Dopov. Akad. Nauk Ukr. RSR* **1962**, 1329.
- [5] P. J. Webster, *J. Phys. Chem. Solids* **1971**, 32, 1221.
- [6] J. Kübler, A. R. Williams, C. B. Sommers, *Phys. Rev. B* **1983**, 28, 1745.
- [7] R. A. de Groot, F. M. Müller, P. G. v. Engen, K. H. J. Buschow, *Phys. Rev. Lett.* **1983**, 50, 2024.
- [8] C. Felser, G. H. Fecher, B. Balke, *Angew. Chem.* **2007**, 119, 680; *Angew. Chem. Int. Ed.* **2007**, 46, 668.
- [9] N. Shutoh, S. Sakurada, *J. Alloys Compd.* **2005**, 389, 204.
- [10] C. S. Lue, Y. K. Kuo, *Phys. Rev. B* **2002**, 66, 085121.
- [11] J. Winterlik, G. H. Fecher, C. Felser, *Solid State Commun.* **2008**, 145, 475.
- [12] H. Ebert, in *Electronic Structure and Physical Properties of Solids – The Use of the LMTO Method*, Lecture Notes in Physics, vol. 535 (Ed.: H. Dreyse), Springer-Verlag, Berlin, Heidelberg, **1999**, pp. 191–246.
- [13] G. E. Bacon, J. S. Plant, *J. Phys. F: Met. Phys.* **1971**, 524.
- [14] P. P. Ewald, C. Hermann, in *Strukturbericht 1913–1928*, vol. I (Eds.: P. P. Ewald, C. Hermann), Akademische Verlagsgesellschaft M. B. H., Leipzig, **1931**, p. 488.
- [15] P. J. Webster, K. R. A. Ziebeck, in *Alloys and Compounds of d-Elements with Main Group Elements, Part 2*, Landolt-Börnstein, Group III (Condensed Matter), vol. 19C (Ed.: H. P. J. Wijn), Springer-Verlag, Heidelberg, **1988**, pp. 104–185.
- [16] U. Eberz, W. Seelentag, H.-U. Schuster, *Z. Naturforsch. B* **1980**, 35, 1341.
- [17] G. H. Fecher, H. C. Kandpal, S. Wurmehl, C. Felser, G. Schönhense, *J. Appl. Phys.* **2006**, 99, 08J106.
- [18] J. Kübler, *Theory of Itinerant Electron Magnetism*, Clarendon Press, Oxford, **2000**.
- [19] I. Galanakis, P. H. Dederichs, N. Papanikolaou, *Phys. Rev. B* **2002**, 66, 174429.
- [20] H. C. Kandpal, G. H. Fecher, C. Felser, *J. Phys. D: Appl. Phys.* **2007**, 40, 1507.
- [21] S. Wurmehl, H. C. Kandpal, G. H. Fecher, C. Felser, *J. Phys. Condens. Matter* **2006**, 18, 6171.
- [22] W. E. Pickett, *Phys. Rev. B* **1998**, 57, 10613.

Received: January 3, 2011
Published Online: July 21, 2011