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Reduction of the substitutional disorder by heat treatments in $Mn_{2-x}Co_xVAl$ Heusler alloys

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Abstract. We report on the preparation and the atomic disorder reduction by annealing in $Mn_{2-x}Co_xVAl$ Heusler alloys. The degrees of the B2 and $L2_1$ atomic ordering for the as-cast samples, obtained from intensity ratios of (200) and (111) peaks respectively related to (220) peak of the X-ray patterns, are significantly improved after annealing at 700 - 800 °C for 72 h. The diminution of the substitutional disorder is essential in these types of compounds, as the half-metallic character and the magnetic properties are primarily influenced by this factor.

Introduction

Heusler alloys are ternary intermetallic compounds of the $L2_1$ structure with stoichiometric composition X_2YZ, where X and Y are usually two different transition metals and Z is a nonmagnetic element [1]. Earlier studies have shown that Mn_2VAl Heusler alloy is a half-metallic ferrimagnet [2-5]. This compound is characterized by an antiparallel coupling between the Mn and V magnetic moments, the total spin moment being 2 μB per formula unit [2, 3]. The high Curie temperature of 760 K [3] makes it interesting for spintronic applications. The spin compensation in $Mn_{2-x}Co_xVAl$ alloy was induced by progressive substitution of Co for Mn and a fully compensated ferrimagnetic behavior has been experimentally obtained for the MnCoVAl alloy [4]. The presence of a considerable atomic disorder in the Mn2VAl compound due to the intermixing of the V and Al atoms has been reported [5]. Previous studies have shown that the magnetic properties and the half-metallic character of these Heusler alloys are strongly influenced by the crystallographic disorder [1, 3, 6, 7]. The aim of the present work is to reduce the substitutional disorder by heat treatments in $Mn_{2-x}Co_xVAl$ Heusler alloys. For the evaluation of the atomic ordering in the full Heusler alloys, the Takamura's model has been used [8]. In order to determine and to adjust the ordering parameters defined in this model, X-ray diffraction (XRD), differential scanning calorimetry (DSC) and neutron diffraction studies have been performed.

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Experimental details

The $Mn_{2-x}Co_xVAl$ (x= 0, 0.2, 0.6, 1) ingots were prepared by induction melting under a purified Ar atmosphere of the starting components Mn (99.95 wt %), Al (99.999 wt %), V (99.99 wt %) and Co (99.99 wt %). An excess of 3 wt % of manganese was added to the stoichiometric mixture in order to compensate for preferential Mn evaporation during the melting processes. The samples were turned and remelted repeatedly in order to ensure homogeneity. The water-cooled copper crucible ensured a rapid cooling of the alloys after melting. The samples were wrapped in tantalum foil, sealed in quartz tubes and subsequently annealed in an Ar atmosphere for 72 hours. The stoichiometry of our as-cast samples was investigated using the energy dispersive X-ray analysis (EDX). The crystal structure of the alloys was investigated at room temperature by using a Brůker D8 Advance diffractometer using Cu Kα radiation. The structural transformations in the 50 – 1000 °C temperature range were identified from differential scanning calorimetry under Ar atmosphere with a temperature ramp rate of 20 °C/min. The cooling was performed at 20 °C/min controlled by forced air cooling (Q600 TA Instruments). The neutron diffraction investigations have been performed at the Institute Laue-Langevin, Grenoble, France, using the high intensity powder diffractometer D1B [9] exploiting the wavelength of 0.128 nm and 0.252 nm respectively, which were selected by Ge and pyrolytic graphite monochromator respectively. The diffraction patterns were indexed by using the FULLPROF program [10].

Results and discussions

The EDX measurements on the as-cast MnCoVAl sample are shown in Fig. 1. The quantity for each element is given in atomic percent which, for ideal MnCoVAl alloy stoichiometry, should be 25 at % for each element. The previous studies showed that 5 wt % excess of Al should be added in order to compensate the weight loss due to the evaporation of Al [11].

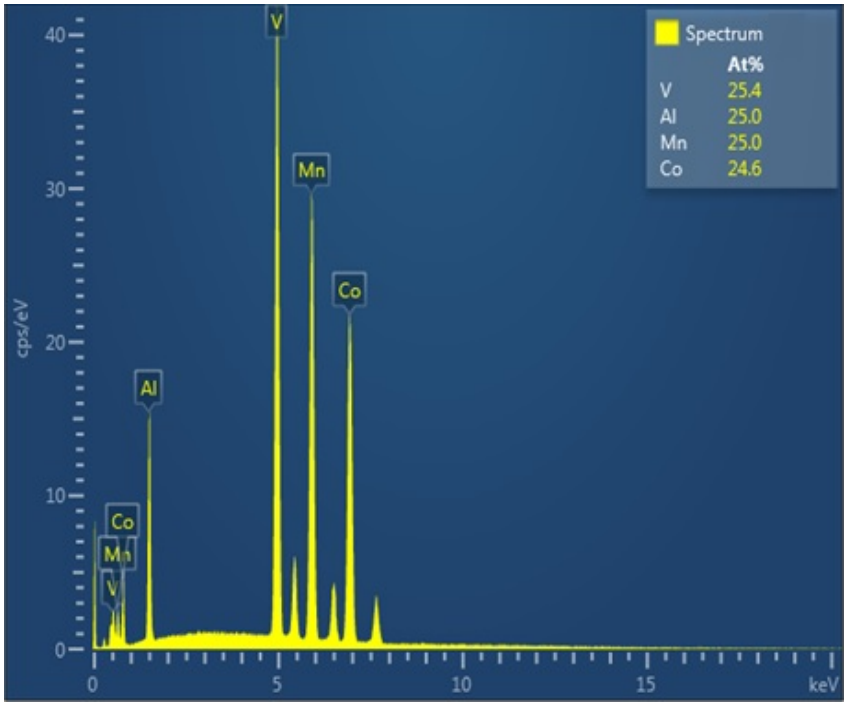

Fig. 1. EDX spectrum of the as-cast MnCoVAl alloy.

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By using no additional Al and by adding 3 wt % Mn, in our samples the weight loss of the final materials is less than 1 wt %. As can be observed in Fig.1, the stoichiometry of our sample is in good agreement with the desired Heusler-type structure, taking into account the measurement errors.

The $Mn_{2-x}Co_xVAl$ alloys crystallize in an ideal full Heusler ($L2_1$) structure (Fig. 2), were the Mn/Co atoms occupy the 8c positions at (1/4 1/4 1/4) and (3/4 3/4 3/4), V occupy the 4a positions at (0 0 0) and Al occupy the 4b positions at (1/2 1/2 1/2) [3].

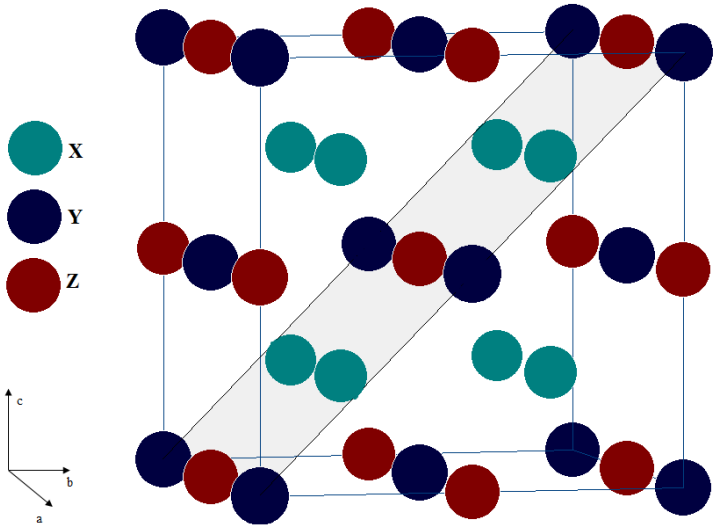

Fig. 2. X_2YZ $L2_1$-type crystal structure of Heusler alloys.

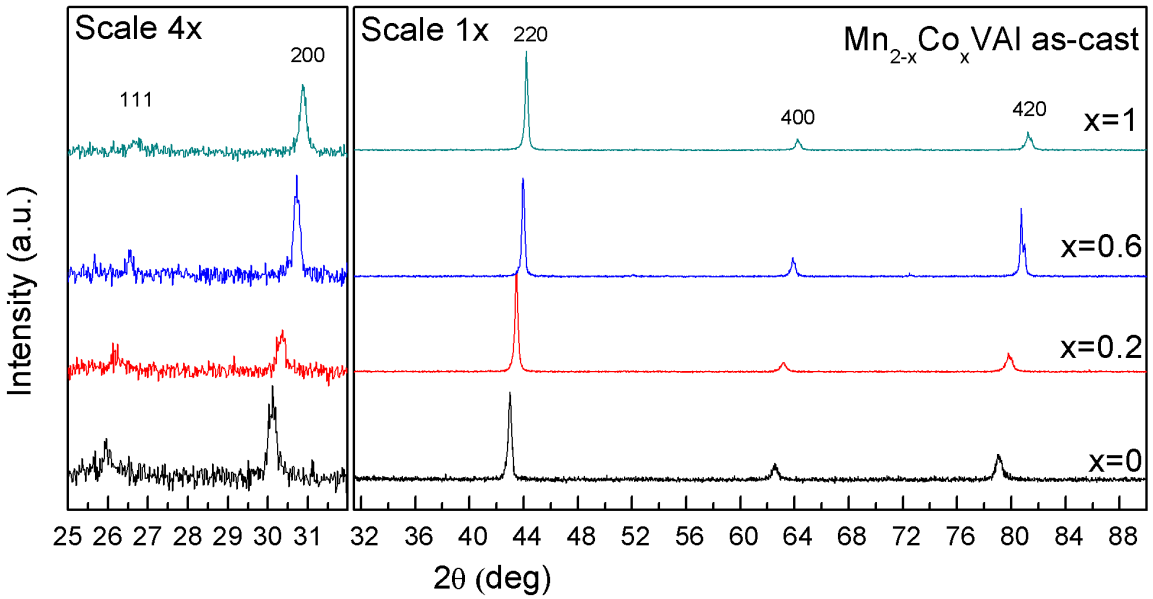

Fig. 3. Room temperature X-ray diffraction pattern of the as-cast $Mn_{2-x}Co_xVAl$ samples. The data are normalized to the intensity of the (220) reflection.

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The X-ray diffraction patterns at room temperature of the as-cast $Mn_{2-x}Co_xVAl$ (x = 0, 0.2, 0.6 and 1) alloys are shown in Fig.3. The XRD patterns prove that the as-cast alloys crystallize in a single phase, corresponding to X_2YZ Heusler type structure, cubic space group $Fm\bar{3}m$ (spatial group no. 225), where the Mn and Co atoms occupy the 8c Wyckoff sites (X), while V and Al atoms are placed on the 4a (Y) and 4b (Z) crystal site, respectively (see Fig.2.). The (111) and (200) superlattice diffraction lines from the XRD patterns prove that all the $Mn_{2-x}Co_xVAl$ alloys exhibit a stable $L2_1$ structure of full Heusler alloys. The extinction of the reflection from the (111) plane indicates an intermixing between the V and Al atoms. Also, if all Mn, V and Al atoms get intermixed, both super-latttice reflections (111) and (200) would disappear [1, 4, 8].

We employed the Takamura's model to investigate the substitutional disorder in our $Mn_{2-x}Co_xVAl$ (x = 0, 0.2, 0.6 and 1) alloys. In this model, two types of ordering parameters have been defined to describe the intermixing between the atomic positions. The S_{B2} order parameter describes the probability of Mn atoms to occupy the X sites (8c) in the X_2YZ full Heusler alloys, being defined:

$$S_{B2} = \frac{n_{Mn\ on\ X} - n_{Mn\ on\ X}^{random}}{n_{Mn\ on\ X}^{full\ order} - n_{Mn\ on\ X}^{random}} \qquad (1)$$

The second order parameter S_{L21} describes the probability of V to occupy the Y position in the X_2YZ full Heusler alloys:

$$S_{L21} = \frac{n_{V\ on\ Y} - n_{V\ on\ Y}^{random}}{n_{V on\ Y}^{full\ order} - n_{V on\ Y}^{random}} \qquad (2)$$

Table 1. Structural parameters including S_{B2} and S_{L21} ordering parameters unit cell constant and the site occupation for the as-cast $Mn_{2-x}Co_xVAl$ samples.

Co content (x)	Atoms	X site	Y site	Z site	S_{B2}	S_{L21}	a_{lat} (nm)
0	*Mn*	1.84	0.08	0.08	0.847	0.60	0.59087
	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	0.68	0.58880
	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	0.52	0.58533
	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	0.52	0.58115
	V	0.07	0.75	0.18			
	Al	0.07	0.18	0.75			

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The S_{B2} and S_{L21} ordering parameters are related to the site occupation in the $L2_1$ structure. Using the Takamura's extended order model for Heusler compounds [8] the S_{B2} and S_{L2} ordering parameters are calculated from the peaks ratios of the XRD patterns as follows:

$$\frac{I_{200}}{I_{220}} = (S_{B2})^2 \frac{I_{200}^{full-order}}{I_{220}^{full-order}} \qquad (3),$$

$$\frac{I_{111}}{I_{220}} = \left[S_{L2_1}\left(\frac{3-S_{B2}}{2}\right)\right]^2 \frac{I_{111}^{full-order}}{I_{220}^{full-order}} \quad (4)$$

where $\frac{I_{200}}{I_{220}}$ and $\frac{I_{111}}{I_{220}}$ are the experimental intensity ratios obtained between (200), (111) and (220) diffraction peaks respectively and $\frac{I_{200}^{full-order}}{I_{220}^{full-order}}$, $\frac{I_{111}^{full-order}}{I_{220}^{full-order}}$ are the diffraction intensity ratios for the ideal structure. The calculated values of S_{B2} and S_{L21} ordering parameters together with the lattice parameters and the site occupation for the as-cast $Mn_{2-x}Co_xVAl$ samples are given in Table 1. Previously we have shown that any changes of these parameters will significantly influence the magnetic and electronic properties of $Mn_{2-x}M_xVAl$ (M = Co or Cu) Heusler systems [6, 7]. As can be seen in Table 1, a substantial degree of mixing between the V and Al is present in all our samples. Also, a smaller but non-negligible intermixing between Mn, V and Al is present on the 8c sites.

In order to decrease the substitutional disorder in our samples, we performed heat treatments. The temperature for the annealing has been settled using the differential scanning calorimetry (DSC) investigations shown in Fig. 4. The DSC curve of Mn_2VAl sample indicates the presence of two new reversible phase transitions (endothermic peaks shown by arrows on heating curve and exothermic peaks on the cooling curve respectively) around 800 ^{o} C. The ordering degree was improved by heat treatment at 700 °C avoiding the above two phase transitions. The DSC curve of MnCoVAl sample doesn't show any phase transitions up to 900 °C, so the heat treatment at 800 °C results in an improving of the ordering parameters for this sample.

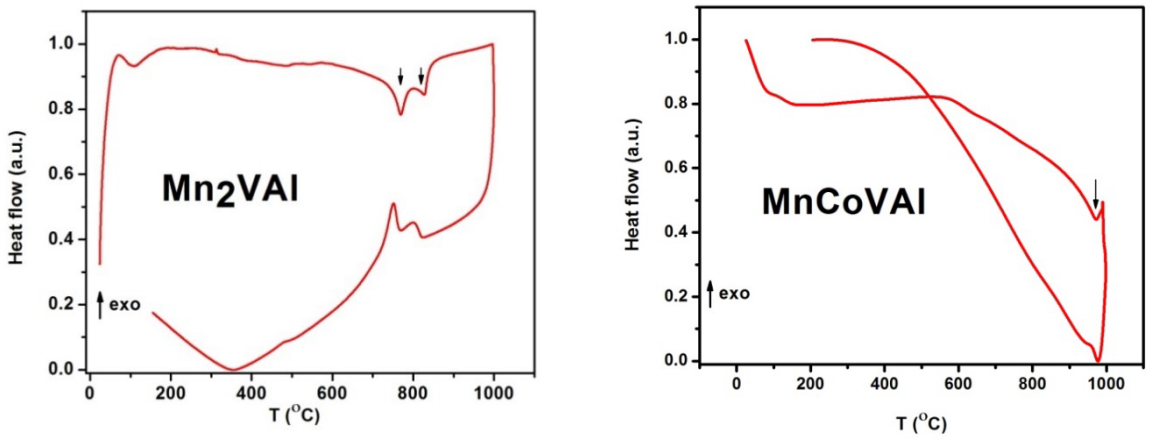

Fig. 4. DSC curves for the Mn_2VAl (left) and MnCoVAl (right) samples.

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The (111) and (200) superlattice diffraction lines from the XRD patterns at room temperature of the annealed $Mn_{2-x}Co_xVAl$ (x = 0, 0.2, 0.6 and 1) alloys are shown in Fig.5. For comparison are given the XRD patterns of as-cast samples. All the annealed samples crystallize in a Heusler type structure ($Fm\bar{3}m$ space group no. 225). The increase of 2θ angle for the diffraction peaks shows the decrease of the lattice parameters after annealing.

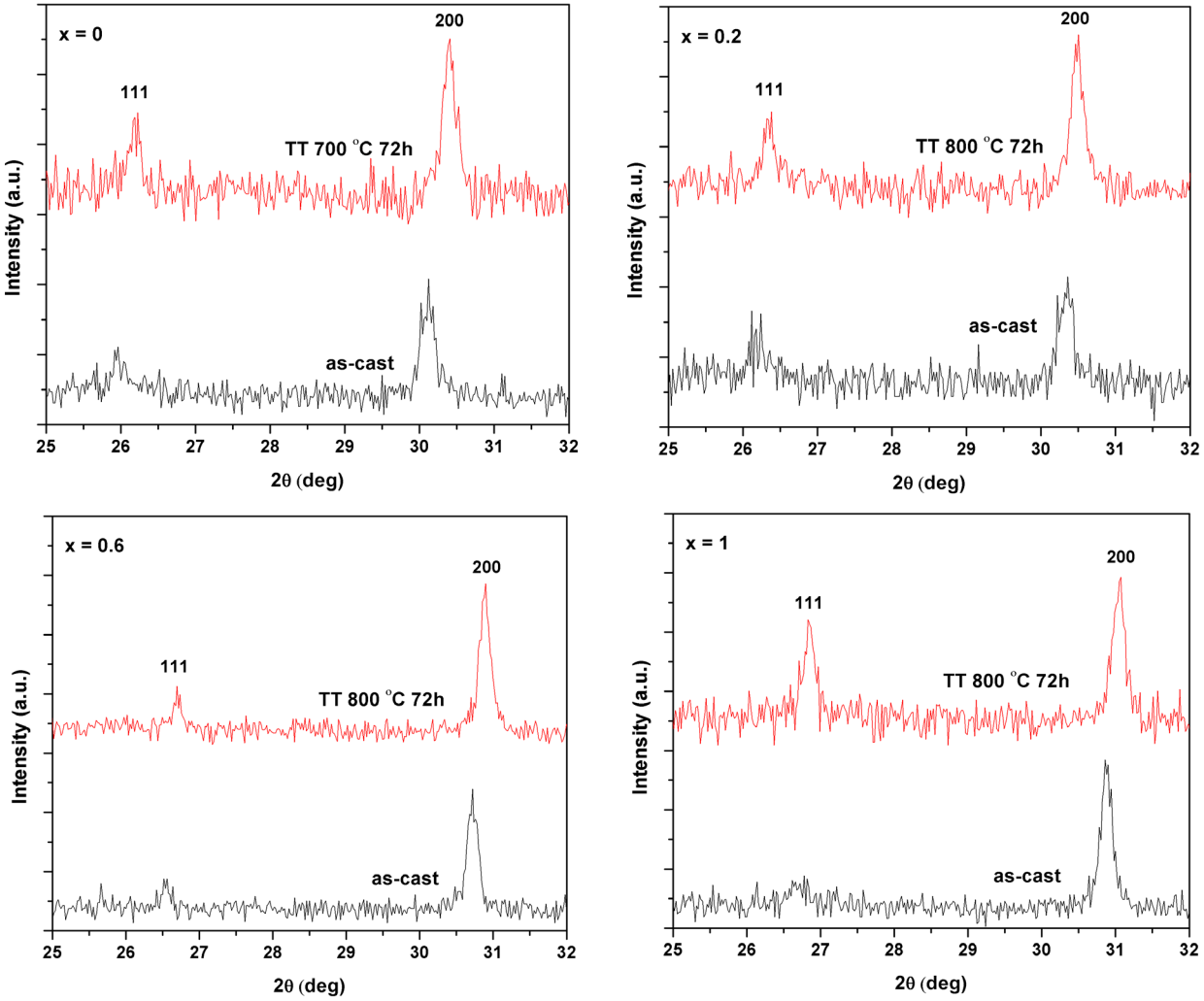

Fig. 5. X-ray diffraction patterns of $Mn_{2-x}Co_xVAl$ as-cast and annealed samples.

The S_{B2} and S_{L21} ordering parameters, lattice constants and the site occupation for the annealed $Mn_{2-x}Co_xVAl$ compounds are shown in Table 2. A substantial increase of the S_{B2} ordering parameter compared with the as-cast samples is observed. Also, the S_{L21} ordering parameters are improved for all the $Mn_{2-x}Co_xVAl$ samples. Accordingly, the probability of Mn and Co atoms to occupy the 8c sites is close to 100%, whilst an intermixing between Al and V atoms is still present for all investigated samples. Therefore, the annealing of the as-cast samples leads to an improvement of the order parameters. The evolution of the lattice constant vs. Co content in the $Mn_{2-x}Co_xVAl$ compounds, both as-cast and annealed samples, is shown in Fig. 6. The variation of the lattice constant vs. Co content in the $Mn_{2-x}Co_xVAl$ alloys is in agreement with the relationship between the Co and Mn metallic radii (r_{Co}=0.125 nm, r_{Mn}=0.127 nm). The monotonous decrease

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of the lattice constant proves that the Co for Mn substitution occurs in the 8c site. The lattice constant follows the same trend for both cases (as-cast and annealed samples) by decreasing with increasing of the Co content. The contraction of the lattice parameter for the annealed samples suggests that the heat treatment increases the order in our samples and reduces the internal stress. Also, the values of the lattice parameter are in agreement with others results reported in literature (5.92 Å) [3,12,13].

Table 2. The lattice parameters, S_{B2} and S_{L21} ordering parameters and the site occupation for the annealed $Mn_{2-x}Co_xVAl$ samples.

Co content (x)	Atoms	X site	Y site	Z site	S_{B2}	S_{L21}	a_{lat} (nm)
0	*Mn*	1.99	0.005	0.005	0.995	0.66	0.58967
	V	0.005	0.83	0.165			
	Al	0.005	0.165	0.83			
0.2	*Mn/Co*	1.99	0.005	0.005	0.997	0.77	0.58765
	V	0.005	0.90	0.095			
	Al	0.005	0.095	0.90			
0.6	*Mn/Co*	1.99	0.005	0.005	0.981	0.59	0.58304
	V	0.005	0.79	0.205			
	Al	0.005	0.205	0.79			
1.0	*Mn/Co*	1.98902	0.00549	0.00549	0.989	0.959	0.58003
	V	0.00549	0.97918	0.01533			
	Al	0.00549	0.01533	0.97918			

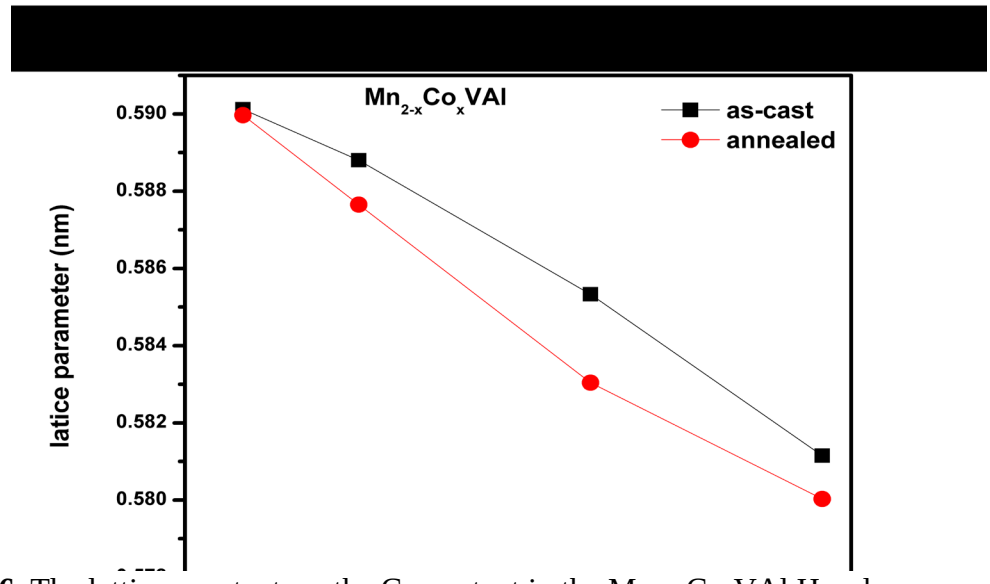

Fig. 6. The lattice constant vs. the Co content in the $Mn_{2-x}Co_xVAl$ Heusler compounds.

The neutron diffraction experiments have been employed in order to investigate the crystallographic structural properties of our samples. The powder neutron diffraction patterns

measured at 300 K for Mn_2VAl (x = 0) for the as-cast sample is given in Fig. 7 as example. The experimental data and the calculated fitting curves are indicated by red dots and solid black lines, respectively, while the blue lines at the bottom show the difference between them. The fitting curves of the Mn_2VAl and MnCoVAl alloys have been calculated by considering the full Heusler structure in cubic space group $Fm\bar{3}m$ (spatial group no. 225). From these preliminary results we may conclude that the neutron diffraction measurements confirm that our samples have a single-phase structure without any impure phases as can be observed also from XRD measurements.

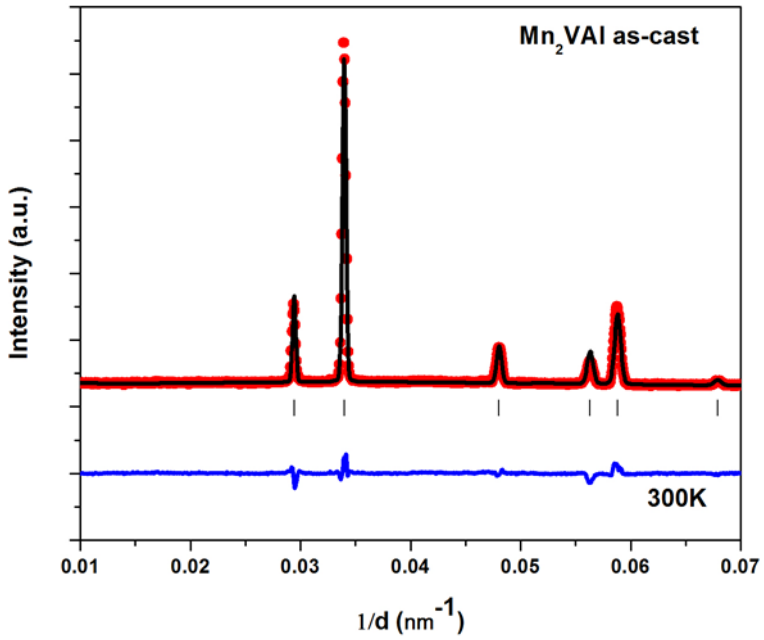

Fig. 7. Room temperature neutron diffraction pattern for the as-cast $Mn_{2-x}Co_xVAl$ sample (x = 0)

Summary

Bulk $Mn_{2-x}Co_xVAl$ (x = 0, 0.2, 0.6 and 1) alloys have been prepared by induction melting. The crystal structure investigated by XRD and neutron diffraction shows that all the analyzed samples are single phases belonging to the stable $L2_1$ (spatial group no. 225) structural order. The degrees of $L2_1$ and B2 order have been calculated from the peaks ratios of the XRD patterns using the Takamura's extended order model for Heusler compounds. Annealing of as-cast samples leads to an increase of the order parameters, which could also be inferred from the reduction of the lattice parameters.

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