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Lattice ordering and magnetic structure of high moment Fe and Co based Heusler alloys prepared by mechanical alloying

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ABSTRACT

Co-based and Fe-based full Heusler compounds with composition $Co_2M'Z$ or $Fe_2M'Z$ (where M' is a transition metal and Z is a main group element) are attracting attention due to their predicted half-metallic behavior, a greatly desired property for spin-dependent electron transport devices. In this work four Heusler compounds (Co_2FeGe, Co_2FeSi, Fe_2CoGe, Fe_2CoSi), have been prepared by mechanical alloying. The effect of vacuum annealing on properties was studied. According to the structural measurements 15 hours milling was enough for crystallization of these compounds. During annealing the crystallite size increased and lattice ordering enhanced. Two superlattice peaks appeared in X-ray pattern due to enhancement of lattice ordering of two Si content compounds. In Co-based compounds the saturation magnetization value increased to a closer value of Slater Pauling model because of improvement of lattice ordering. The value of M_s in some Fe-based compounds was higher than that predicted by Slater Pauling model.

1. Introduction

Heusler alloys with the chemical formula X_2YZ have attracted substantial interest because of their exceptional physical properties [1]. High moment ferromagnetic iron and cobalt-based Heusler alloys have attracted considerable attention for their potential use as applicable materials in the field of spin-electronics and magnetoresistive devices [2,3]. Ferromagnetic Co_2-Heusler compounds, are candidate materials for spintronic memory and sensor applications. A number of high-performance Co_2-Heusler compounds have already been reported as ferromagnetic electrodes in magnetic tunnel junctions (MTJs), current-perpendicular-to-plane giant magnetoresistive (CPPGMR) devices, and lateral spin-valve (LSV) devices [4,5]. Lattice ordering is one of the most important factors in determination of properties of Heusler alloys [1]. A fully ordered atomic arrangement in Heulser alloys is the $L2_1$ structure, however, the partially disordered B_2 and fully disordered A_2 structures also exist [1]. The electronic structure plays an important role in determining the magnetic properties of Heusler compounds and, in particular, for predicting half-metallic ferromagnetism. The Slater–Pauling curve [6,7] is a simple way to study the interrelation between the valence electron concentration and the magnetic moments in ferromagnetic Heusler alloys. For ordered Heusler compounds, one has to subtract 24 from the accumulated number of valence electrons in the unit cell (N_v) to find the magnetic moment per unit cell (m): $m = N_V - 24$. With N_V denoting the accumulated number of valence electrons in the unit cell containing four atoms.

Usually, the results of the band structure calculations are close to Slater Pauling prediction [8].

In experimental field, scientists try to control the lattice ordering during the preparation of these compounds. Extending of preparation method is one of the results of these attempts. Polycrystalline Heusler samples were usually synthesized by arc-melting of elements in a noble gas atmosphere. The mechanical alloying (MA) route has been recognized as a powerful method for the production of novel, high-performance and low-cost materials such as ferrites, manganites, intermetallic and Heusler alloys [9–14].

Recently Hatchard et al. [15] have explored MA technique for processing of Ni–Mn–Ga Heusler alloys.

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Vinesh et al. [16] investigated the effect of ball milling on magnetic properties of Fe_2MnAl Heusler alloys. Also, Ren and his coworkers [17] synthesized Fe_2CoGe by ball-milling and studied its structure and magnetic properties. In previous work [18] we studied the evolution of microstructural and mechanical properties of nanocrystalline Co_2FeAl alloy during ball milling. In that work high moment ferromagnetic iron and cobalt based Heusler alloys have been made by MA and X-ray diffraction and Mössbauer have been used to study the effect of vacuum annealing on lattice ordering and magnetic properties.

In this research the high saturation magnetization is of interest from the practical point of view. We tried to produce Heusler compounds with the highest possible saturation magnetization. The construction method has also been changed to check its effect on this goal. Also, substituting elements by changing the distance of the bonds has an effect on the type and strength of the interaction. On the other hand, the effect of electron injection or electron reduction to the device is also significant in these compounds. Here, an attempt has been made to produce experimental data by applying these changes. These data can be used in theoretical and simulation studies and which lead to more knowledge of these compounds.

2. Experimental details

Co_2FeM and Fe_2CoM (M=Ge, Si) alloys were made by mechanical alloying. The initial elements were mixed and ball milled in a high-energy mill for 15 hours. For the investigation of the effect of annealing, part of samples was annealed in sealed quartz tubes for 48 hours at 1000 °C. All samples were characterized by X-ray diffraction and magnetization measurements in a 5 T SQUID magnetometer. The powder magnetoresistance, PMR, measurements were carried out by the four-probe method in the magnetic field of range of 0 – 1T. The crystal structure of the samples was examined by X-ray diffraction (XRD) at room temperature using $CuK\alpha_1$ and $CuK\alpha_2$ radiations. The crystal structures were refined by Rietveld analysis. The magnetic properties were measured by a vibrating sample magnetometer(VSM) at room temperature. We used Zeiss ULTRA plus SEM for analyzing samples.

3. Results and discussion

Fig. 1. shows the Rietveld refinement of Co-based samples before and after annealing. Also, Figure 2 shows the Rietveld refinement of Fe-based samples before and after annealing. The structural results are summarized in Table 1. It seems that 15 hours milling is enough to obtain a single phase spectrum in all samples. A crystallite size in the range of about 10nm estimated from the Scherrer broadening for all ball milled samples. During annealing, this parameter has increased up to 6 and 4 times higher value for Si and Ge content samples respectively. Also, lattice ordering has improved by annealing. Apart from Co_2FeGe, which has the L21 structure, all the samples seem to be crystallized in a disordered W-type structure. Annealing cause, the atoms to propagate in those preferred positions in L21 structure.

The ordered Co_2FeSi and Fe_2CoSi samples is identified by the occurrence of the fcc-typical (111) and (200) reflections, and their relation to the (220) reflection. However, the intensity of these two common fcc reflections in Co_2FeGe and Fe_2CoGe compounds is very low. This is, in particular, the case, if all elements contained in the compound have a similar atomic number. Unfortunately, the intensity of the (111) and the (200) reflections can then be below 1% of the scattered intensity of the (220) reflection, which almost leads to the disappearance of the (111) and the (200) reflections. In these cases, XRD is not a good method for investigation of lattice ordering.

Lattice parameter of the Co_2FeSi samples before and after annealing was 569.0 and 564.5 pm respectively. [19,20]. The lattice parameter of the Fe_2CoSi is also reported as 564 pm [21]. Also, the lattice parameter of four Ge content samples was in good agreement with previous works [22,17].

Magnetic hysteresis loop of the Co-based samples measured at 4 and 300K is shown in Figure 3. All 4 samples show a soft magnetic behavior. Also, hysteresis loop of the Fe-based samples is shown in Figure 4 similar behavior can be seen. Insets show the M-T curves measured in a field of 1T. As can be seen, there is a little decrease of magnetization with increasing of temperature. All of these samples have a high magnetic moment and high curie temperature. In other work, a decrease of a range of 1% from 4 to 300K is reported [23]. Saturation magnetization of the samples is summarized in Table 1. For comparison with Slater Pauling model, a value in μ_B/F.u. is also reported. As expected the M_s value at 4K is slightly higher than at 300K. The saturation magnetization of Co_2FeSi before annealing is 5 μ_B. According to Slater-Pauling model it should be 6 μ_B. After annealing, this parameter increases to 5.92 μ_B. Kumar et al. [22] obtained 5.58 and 6 μ_B/F.u. for saturation magnetization of this compound by GGA and GGA+U calculation respectively. On the other hand, experimentally obtained values are in the range of 5.18-5.97 μ_B/F.u. for this parameter [22]. It seems that Slater Pauling prediction is in a best agreement with actual value of M_s for this compound. The difference between experimental data relates to the different value of disorder in the samples. Also, the presence of some areas with very high amount of disorder in the grain boundaries can be contributed to the reduction of saturation magnetization in the milled sample.

Co_2FeGe has a similar behavior. The difference is that the saturation magnetization for annealed sample is higher than that obtained from applying Slater Pauling. According to our best finding, the maximum value of the saturation magnetization in experimental reports is 5.9μ_B/F.u. [24]. This deviation is more prominent in Fe based samples and most of those have a saturation magnetization value higher than that predicted Slater Pauling method.

Also, powder magnetoresistance (PMR) of the samples was measured. For this measurement, the powders were pressed into a rectangular cube of 1mm width, 1mm height and 10mm length. The powder was mixed with various amounts of MgO powder to bring the mixture closer to the percolation threshold. The powder magnetoresistance was measured at room temperature for pressed samples. However, in no case were we able to measure PMR in excess of 1%.

Table 1. Saturation magnetization of the samples. (m:15 hours Milled and ma:15 hours Milled +48 hours Annealed at 1000^{o}C) and structural parameters results from Rietveld refinement (To convert Am_2/kg to μ_B/F.u we used the relationship $M(A/1000)/(\mu_B)(N_A)$. That M is magnetic moment in Am_2/kg, A is mass number, μ_B is equal 9.27exp-24 and N_A is equal 6.02exp23.

Compound	N_v	Magnetic moment [Am_2/kg] 300K(4.2K)	M[μ_B/F.u.] 300K (4.2K)	Structure	Crystallite size (nm)	Lattice parameter (Pm)
Co_2FeSi(m)	30	133.2 (138.6)	4.82 (5.02)	A_2	8	569.0
Co_2FeSi(ma)	30	157.0 (163.7)	5.68 (5.93)	$L2_1$	47	564.5
Co_2FeGe(m)	30	86.3 (96.4)	3.82 (4.27)	$L2_1$	6	572.5
Co_2FeGe(ma)	30	128.3 (134.6)	5.68 (5.96)	$L2_1$	37	574.3
Fe_2CoGe(m)	29	109.9 (117.9)	4.81 (5.15)	A_2	9	574.4
Fe_2CoGe(ma)	29	221.5 (230.2)	9.68 (10.07)	B_2	37	573.1
Fe_2CoSi(m)	29	144.6 (150.7)	5.16 (5.37)	A_2	9	570.8
Fe_2CoSi(ma)	29	158.6 (160.9)	5.66 (5.74)	$L2_1$	59	564.6

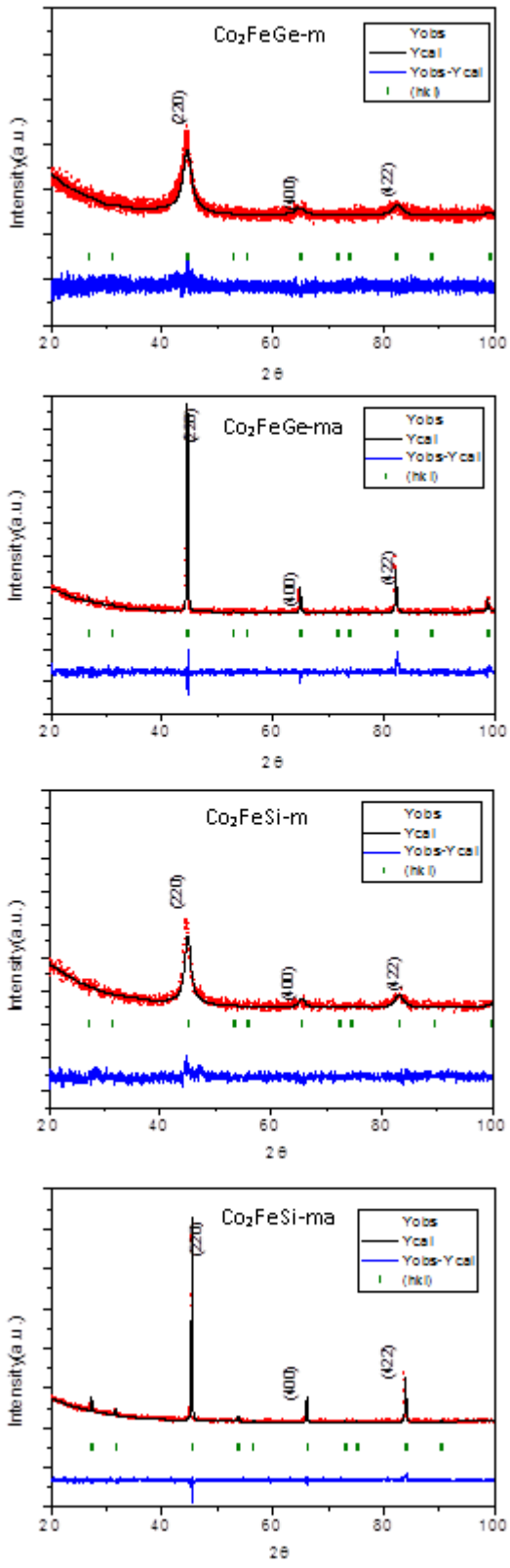

Fig.1. The Rietveld refinement for the Co-based samples

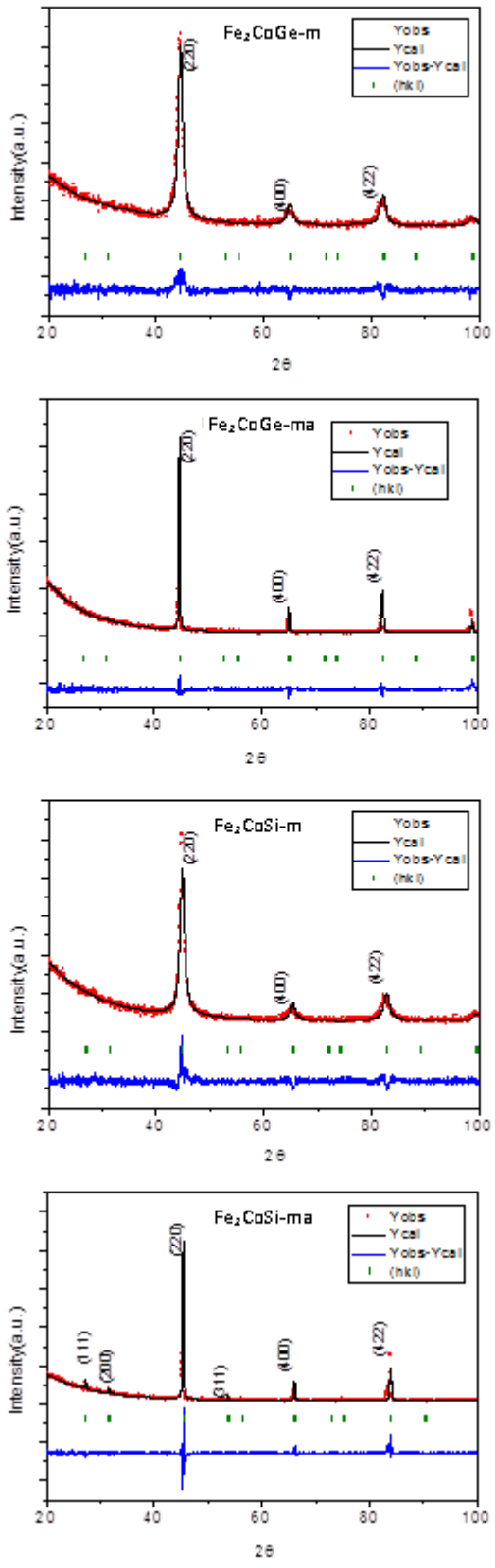

Fig.2. The Rietveld refinement for the Fe-based samples

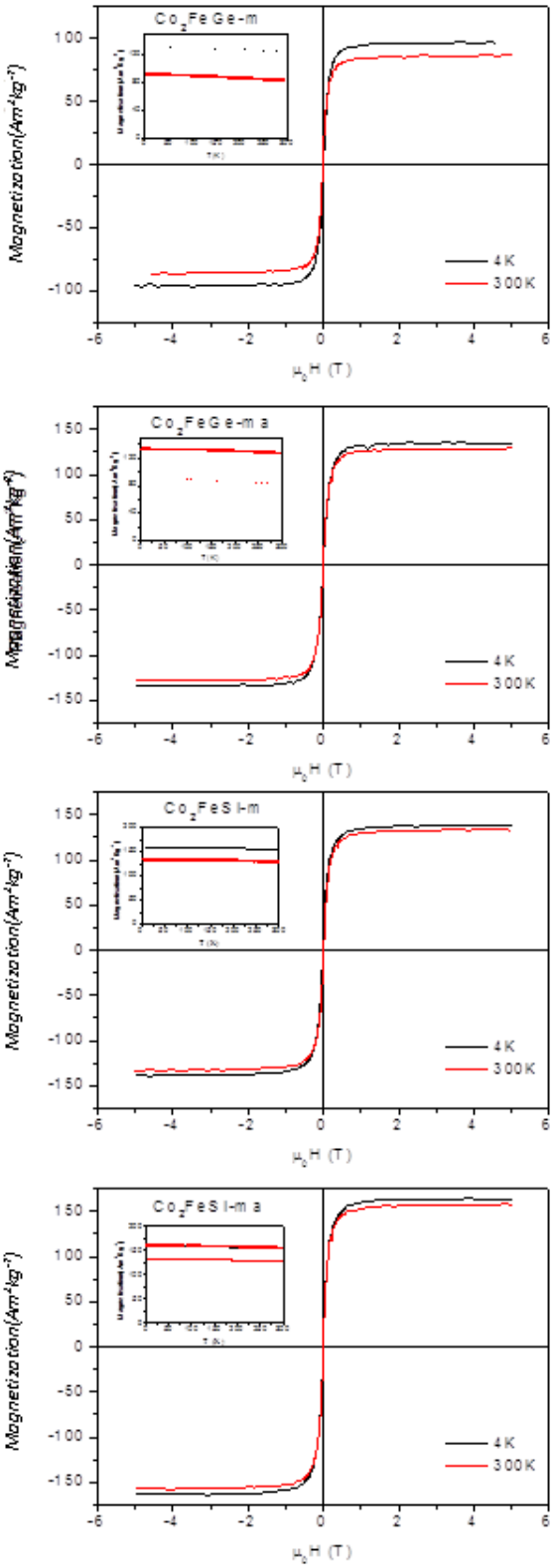

Fig.3. Magnetic hysteresis loop of Co-based samples measured at 5 and 300 K (inset shows M-T curve measured at 1T)

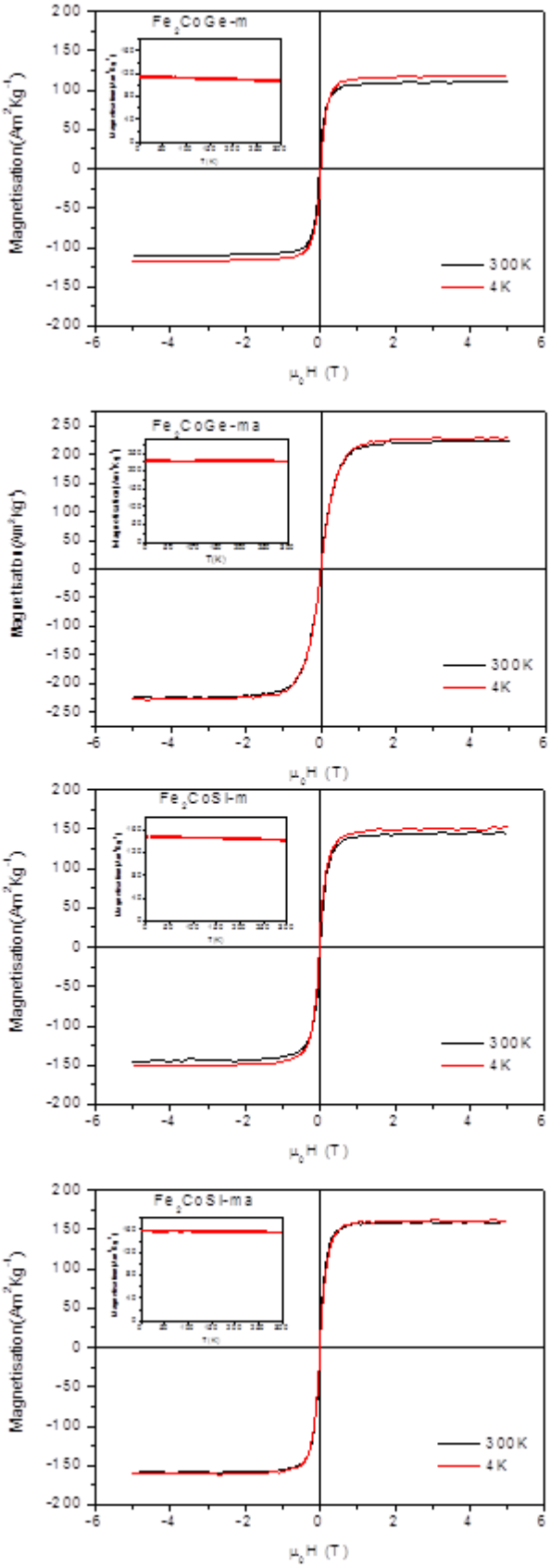

Fig. 4. Magnetic hysteresis loop of Fe-based samples measured at 5 and 300 K (inset shows M-T curve measured at 1T)

4. Conclusion

Four Heusler compounds (Co_2FeGe, Co_2FeSi, Fe_2CoGe, Fe_2CoSi) have been prepared by mechanical alloying. The effect of vacuum annealing on their properties was studied. According to the structural measurements 15 hours milling was enough for crystallization of these compounds. During annealing the crystallite size increased and lattice ordering enhanced. Two superlattice peaks appeared in X-ray pattern due to enhancement of lattice ordering of two Si content compounds. In Co based compounds the saturation magnetization value increased to a value close to that obtained by applying Slater Pauling model because of improvement of lattice ordering. The value of M_s in some Fe based compounds was higher than that predicted by Slater Pauling.

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