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Magnetic Properties of Co_2MnSi Compound with Tb Impurities

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In this paper we report our experimental and theoretical studies on the effect of Tb impurity on the magnetic properties of the Heusler half metallic ferromagnet Co_2MnSi. The analysis of the band structures of the doped alloy shows that the half-metallic properties are completely conserved if Tb substitute Mn atoms, this effect being determined through the coupling between the R($4f$) spin with the Mn($3d$) itinerant electron spins. We evaluate the strength of such a coupling by calculating, in an *ab initio* fashion, the total energy of $Co_{16}Mn_7TbSi_8$ compound for a parallel and antiparallel $f-d$ coupling. The experimental magnetic moments are in good agreement with the calculated ones in case of ferrimagnetic ordering.

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1. Introduction

The Heusler alloys containing Co and Mn are amongst the most extensively studied half metallic ferromagnets [1]. Half-metallicity was predicted by de Groot [2], when studying the band structure of half-Heusler NiMnSb alloy. Later on Kubler et al. [3] recognized that minority spin states in Co_2MnAl nearly vanish, so the way in investigating the full-Heusler alloys having Co_2MnZ (Z = Al, Si, and Ge) was opened. These alloys crystallize in a highly ordered $L2_1$ structure, which belong to $Fm\bar{3}m$ space group. Co_2MnSi attracted particular interests because of its high Curie temperature 985 K and a gap of 0.4 eV in the minority spin channel [4, 5]. Structural and magnetic properties of Co_2MnSi alloy were reported. A magnetic moment of 5.01 μ_B/f.u. was shown [6].

Sakuraba et al. [7] have fabricated magnetic tunnel junctions (MTJ) consisting of highly ordered Co_2MnSi epitaxial bottom electrode, Al–O tunnel barrier, and $Co_{75}Fe_{25}$ top electrode. A tunnel magnetoresistance (TMR) ratio of 159%, at low temperatures and a value of 70% at room temperature, was determined. More recently, MTJ structures consisting of Co_2MnSi/Al–O/ Co_2MnSi were fabricated, having a TMR ratio of 570%, at 2 K, the largest one reported to date for an Al–O amorphous tunneling barrier [8]. These experiments reveal the HMF character of Co_2MnSi with a minority-spin band gap and a high decrease of TMR ratio with temperature [9].

In all metallic ferromagnets the interactions between spin fluctuations and the conduction electrons are essential in the determination of their physical properties. In the case of half metallic ferromagnets the spin-flip phenomena or one magnon scattering processes are absent due to the presence of the gap in one spin channels [1, 10]. Several results on half metallic or semi-Heusler compounds showed that electronic correlations play a crucial role in depolarization effects by introducing non-quasiparticle states just above the Fermi level [11–14]. Attema et al. [15] have proposed to increase the magnetic anisotropy and thus the magnon gap by doping with rare-earth atoms in the half metallic material due to the impurity R($4f$)–Mn($3d$) coupling, possibly preserving the half-metallic gap. A large $3d$–$4f$ coupling was obtained for the case of Nd substitution, and the weakest coupling was realized in the case of Ho in $NiMn_{1-x}R_xSb$ compounds, with R = Nd, Pm, Ho, and U [16].

Previously we have studied the effect of holmium substitution on Mn sites on the basis of self-consistent electronic structure calculations [17]. It was suggested that Ho can enter in Co_2MnSi lattice. In this paper we analyse the effect of Tb substitution at Mn sites on the physical properties of Co_2MnSi based alloy. The Tb $4f$ electrons are not involved in chemical bonding. Total energy calculation allow us to evaluate the strength of the coupling between the $4f$ rare earth impurity spin and the $3d$ manganese conduction electron spin.

2. Experimental details

The $Co_2Mn_{1-x}Tb_xSi$ compounds with x = 0, 0.01, and 0.05 and 0.1 were prepared by arc melting the constituent elements in a purified argon atmosphere. The ingots were remelted several times in order to ensure a good homogeneity. The samples were heat treated in vacuum, at 1000 °C, for 5 days. The crystal structure

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was checked by X-ray using a Bruker 8 XD diffractometer. Magnetic measurements were performed with a 12 T VSM magnetometer from Cryogenics in the temperature range 4.2–700 K and maximum external fields up to 12 T. The spontaneous magnetizations, M_s, were determined from magnetization isotherms according to approach to saturation law: $M = M_s(1-b/H)+\chi_0' H$. We denoted by b the coefficient of magnetic hardness and χ_0' is a Pauli-type contribution.

Based on experimentally determined lattice constants, we have computed the band structures of $Co_2Mn_{0.875}Tb_{0.125}Si$ and Co_2MnSi compounds using a supercell eight times greater than unit cell. A $d-f$-type model was used in the mean field approximation, in which the Mn $3d$ and Tb $4f$ states were described by LSDA+U method, whereas the $3d-4f$ interaction was treated as perturbation. The mean-field Hamiltonian can be written in the form: $H \approx H_{\mathrm{LDA+U}} - J\sum \sigma_i^{3d} S_{i+\delta}^{f}$, where the spin of the conduction electron at site R_i is denoted by σ_i^{3d} and $S_{i+\delta}^{f}$ represents the spin of the $4f$ shell at the $R_{i+\delta}$ site. LSDA+U approach is based on the local spin density approximation (LSDA) to density functional theory (DFT) using exchange-correlation parameterization of von Barth and Hedin but is complemented with Hubbard-U corrections treated in a mean field approximation. Our calculations use a full-potential linearized muffin-tin orbital (FP-LMTO) approach. This method uses an optimized basis set consisting of muffin-tin orbitals with smoothed Hankel functions as envelope functions [14]. The partially filled and strongly correlated localized f orbitals were treated using the LSDA+U method. In this method the Coulomb and exchange energy in the Hartree–Fock approximation of a chosen set of localized orbitals, here the $4f$ states, are added to the usual local spin density functional and their orbital independent average is subtracted to avoid double counting.

3. Results and discussions

The diffraction patterns for the samples with $x = 0.01$ are presented in Fig. 1. Similar diffraction patterns were obtained for all samples. The X-ray analysis shows, in the limit of experimental errors, that the compounds are single phase with BiF_3-type structure, space group no. 225 (according to *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* [18]), for the compounds with $x = 0.00$ and 0.01. The prototype compound in our case is Cu_2MnAl which show no degree of disorder between Co and Mn sites. We have to mention that a low degree of disorder cannot be excluded but this is not detectable by standard XRD. The compounds with $x = 0.05$ and $x = 0.1$ were found to be not single phase, small quantity of Co_2Si_2Tb phase being present. The alloys crystallize in a cubic structure having $Fm\bar{3}m$ space group. The lattice parameter is $a = 0.5653 \pm 0.001$ nm and is very little affected by substitution, probably due to the low Tb concentrations. It was found that the linewidths of the X-ray patterns are somewhat larger

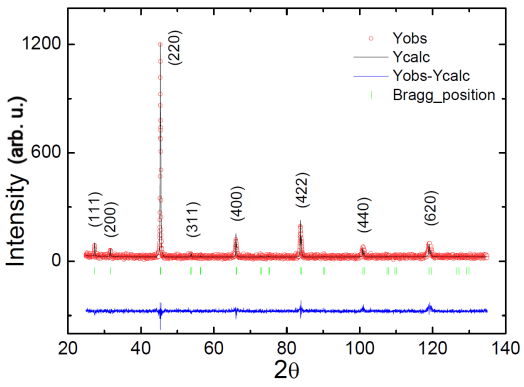

Fig. 1. Diffraction patterns for the $Co_2Mn_{0.99}Tb_{0.01}Si$ compound (Rietveld refinements with the FullProf program was used for fitting the XRD data).

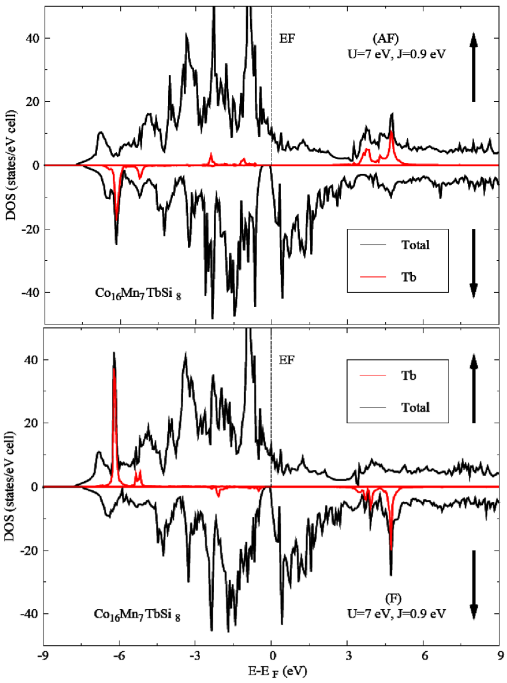

Fig. 2. Density of states for $Co_{16}Mn_7TbSi_8$ compound calculated for $U = 7$ eV in the cases of antiferromagnetic and ferromagnetic coupling.

for the compound with $x = 0.1$ as compared with samples with less Tb. This behaviour could be attributed to a small deformation of the lattice as the Tb content increases.

Previously there were performed calculations for different values of the average Coulomb interaction parameter U [19]. For all U values a half-metallic solution was obtained with a minority gap having similar width as in the spin polarized LDA calculation. Depending on the strength of U the Fermi level moves toward the middle of the gap. It was found no significant dependence in the studied range of the U parameter between 8–12 eV. In the same time a slight modification of the magnetic moment was found. Therefore, in the following calculations, we take the values $U = 7$ and 9 eV and $J = 0.9$ eV for the

Coulomb and exchange parameters, which agrees with the values reported in literature for metallic rare-earth compounds [20].

The calculated densities of states (DOS), for $U = 7$ eV in the case of $Co_{16}Mn_7TbSi_8$ compound are presented in Fig. 2. The calculations were done considering a ferromagnetic, respectively antiferromagnetic coupling of Tb ($4f$) and Mn ($3d$) spins. No important differences can be seen in the DOS calculated with $U = 9$ eV compared with the results for $U = 7$ eV. The analysis of the band structures of the doped alloy shows that the half-metallic properties are not affected if terbium atoms substitute the manganese ones. This effect is not determined by the spin–orbit interaction, but through the coupling between the Tb ($4f$) spin with the Mn ($3d$) itinerant electron spins. We evaluate the strength of such a coupling by calculating, in an *ab-initio* fashion, the total energy of $Co_{16}Mn_7TbSi_8$ compound for a parallel and antiparallel $f-d$ coupling. Given the geometry of the cell, the lanthanide substitution is realized in the fcc-Mn sublattice, so 12 pairs of Tb ($4f$)–Mn ($3d$) are formed. As a consequence the $f-d$ coupling constant was calculated as the $E_{\text{ferro}}-E_{\text{antiferro}}$ energy corresponding to a pair and has values of 58.9 K for $U = 9$ eV, $J = 0.9$ eV and 48.3 K for $U = 7$ eV, $J = 0.9$ eV. One can see that the minimum energy is in the case of an antiparallel coupling between Mn ($3d$) and Gd ($4f$) spins as it is expected for heavy rare-earths $3d$ transition metals compounds [21]. We expect that at temperatures lower than that calculated for the exchange coupling the Tb substitution could affect the magnonic excitations leaving the half metallic gap unmodified. In Table there are presented the atomic magnetic moments for the pure compound and data calculated for the Tb-doped samples in both cases. A modification of Co moment is shown, as result of doping effect. One can see that a small negative moment was found on silicon due to the hybridization effects.

TABLE

Calculated magnetic moments for $Co_{16}Mn_8Si_8$, respectively $Co_{16}Mn_7TbSi_8$ compounds.

U [eV], J [eV]	9; 0.9		7, 0.9		
Coupling	F	AF	F	AF	
Co_1 [μ_B/atom]	1	0.805	0.804	1.087	1.086
Co_2 [μ_B/atom]	1	0.805	0.804	0.808	0.799
Mn [μ_B/atom]	3.03	3.044	3.045	3.044	3.046
Tb [μ_B/atom]	–	5.942	−6.116	5.924	−6.088
Si [μ_B/atom]	−0.03	−0.064	−0.065	−0.064	−0.065
M [μ_B/8f.u.]	40.00	41.919	29.869	41.923	29.847
M/8 [μ_B/f.u.]	5.00	5.239875	3.733625	5.240375	3.730875
E_{tot} [eV]	−8458.7589	−88762.4064	−88762.4109	−88762.4155	−88762.4191
$E_{\text{ferro}} - E_{\text{antiferro}}$ [K]			58.96912039		48.31427775

The magnetization isotherms show saturation in external field of 12 T. From the magnetization isotherms at 4 K the spontaneous magnetizations were determined. The experimental values of the magnetic moment per formula unit (f.u.) measured at 4 K are 5.07, 4.71 and 4.49 μ_B/f.u. for $x = 0.0$, 0.05, and 0.10, respectively. The magnetization values of the doped compounds are smaller than that of parent sample and decrease with the increase of the Tb content. This suggests that the Tb magnetic moments are antiparallel oriented to the transition metals ones, the doped compounds being ferrimagnetically ordered. Considering that the magnetic moments per atom of Co, Mn, Tb, and Si are the same like that calculated in the $Co_{16}Mn_7TbSi_8$ compound, we have calculated the magnetic moments for the doped compounds. The calculated magnetic moments per formula unit are 5.00 μ_B for Co_2MnSi and 4.13, 3.67 μ_B for $x = 0.05$, 0.10 ($U = 9$ eV); 4.41, 3.95 μ_B/f.u. for $x = 0.05$, 0.10 ($U = 7$ eV) for doped samples in the case of antiferromagnetic coupling, respectively.

There is good agreement between the calculated values in case of antiferromagnetic coupling and experimental values. The best agreement is for the results obtained from theoretical calculations considering $U = 7$ eV. Further investigations are necessary in order to find the lattice site occupied by rare earth atoms, the spin–orbit contribution, the dynamics effects and the spin polarizations.

4. Conclusions

The electronic structure calculations suggest that the half-metallicity is preserved when Tb substitutes Mn sites. A rather good agreement between experimental and computed values was obtained for an antiparallel orientation of rare earth and transition metals moments. The best agreement with experimental data was obtained for the calculated values obtained by considering $U = 7$ eV.

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