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Dedicated to Academician Professor Dr. Emil Burzo on His 80th Anniversary

STRUCTURAL, MAGNETIC AND ELECTRONIC PROPERTIES OF THE INTERMETALLIC COMPOUNDS FROM THE TERNARY SYSTEM Ce – Co – Mn

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ABSTRACT. XRD, magnetic and XPS measurements of the three classes of intermetallic compounds with different crystallographic structures are reported. XPS spectra of $Ce_2Co_{15}Mn_3$, $CeCo_7Mn_5$ and $CeCo_8Mn_4$ compounds pointed out the intermediate valence state of Ce atoms and that both Co and Mn atoms carry magnetic moments. The complex magnetic structure is determined by the competition between the ferromagnetic (Co–Co pairs) and antiferromagnetic (Co–Mn and Mn–Mn pairs) interactions. In CeCoMn, $Ce_3Co_3Mn_4$ and Ce_3Co_6Mn compounds both Ce and Co atoms are non-magnetic like in the isostructural compound $CeCo_2$. Magnetic behavior is mostly due to the Mn moments and depends essentially on the Mn - Mn distances.

Keywords: *Mn-Co-Ce intermetallics, XPS, local moments, intermediate valence*

INTRODUCTION

The problem of local moments confined to the transition metals (T) sites, i.e., localized behavior in some aspects of itinerant electrons, is one of the most important issues in the physics of the magnetic alloys and intermetallic compounds [1–3]. The electronic 3d band of the transition metals is determined by the overlap between the d orbitals of adjacent atoms and depends on the number of nearest-

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neighbors and on the hopping integral, which is very sensitive to the T–T distances [4]. The Mn-based alloys and compounds are assumed to exhibit a strong dependence of Mn-Mn exchange interaction as a function of distance between the nearest neighbor Mn atoms. It is well known that the Mn-Mn interaction is antiferromagnetic when the distance d_{Mn-Mn} is smaller than 2.8 Å [5].

On the other hand, in a large number of intermetallic compounds based on Ce and 3d-transition elements was observed a variety of anomalous behaviors in the lattice constants and magnetic properties due to the intermediate valence state of Ce ions [6–11]. Furthermore, the reported experimental data have shown the $CeCo_2$ compound is an exchange-enhanced Pauli paramagnet with a spin fluctuation temperature T_{sf} higher than room temperature and this is consistent with the almost temperature independent magnetic susceptibility below room temperature, indicating that in this compound both Ce and Co atoms are non-magnetic. [12-14].

In the ternary metallic system Ce–Co–Mn, many intermetallic compounds with different crystallographic structures are reported [15]. The aim of this paper is to study the magnetic state of Ce, Co and Mn atoms, the nature and the intensity of the magnetic interactions in the six compounds from this intermetallic system and how these interactions depend on the number of magnetic ions in the unit cell by correlating the results obtained from XRD data, magnetic measurements and XPS spectra. Results on the individual classes of these compounds were published elsewhere [16-18]

EXPERIMENTAL

The intermetallic compounds $Ce_2Co_{15}Mn_3$, $CeCo_8Mn_4$, $CeCo_7Mn_5$, CeCoMn, $Ce_3Co_3Mn_4$ and Ce_3Co_6Mn were prepared in a cold crucible induction furnace under a purified argon atmosphere. The samples were melted repeatedly in the same atmosphere to ensure homogeneity. The purity of the starting materials was 99.9% for all the constituent elements. The crystalline structure of the samples was analyzed at room temperature by using a D 5000 Brücker Bragg-Brentano diffractometer with Cu Ka radiation. The XPS spectra were recorded using a PHI 5600ci ESCA spectrometer with monochromatized Al Ka radiation at room temperature. The magnetic measurements were performed in the temperature range 4 - 550 K and in magnetic field up to 12 T using a vibrating sample magnetometer or by extraction method.

RESULTS AND DISCUSSION

X-Ray diffraction (XRD) measurements showed that all the investigated compounds are single phases. The crystalline structure and the lattice parameters are as follows: $Ce_2Co_{15}Mn_3$ - Th_2Zn_{17} structure type, a = 8.410 Å, c = 12.328 Å, $CeCo_7Mn_5$

and $CeCo_8Mn_4$ - the $ThMn_{12}$ structure type, a = 8.496 Å, c = 4.748 Å and a= 8.464 Å, c = 4.743 Å, respectively and CeCoMn, $Ce_3Co_3Mn_4$ (or $CeCoMn_{1.33}$) and Ce_3Co_6Mn (or $CeCo_2Mn_{0.33}$) - the $MgCu_2$ structure type, a = 7.30 Å, a= 7.33 Å and a= 7.16 Å, respectively, the last three compounds being isostructural with the parent compound $CeCo_2$ with lattice parameter a = 7.16 Å. By the Rietveld refinement one took into account that the atomic sites with a larger Wigner Seitz volume are expected to be preferentially occupied by Mn atoms, since the atomic radius of Mn atoms is larger than that of Co atoms (1.307 Å and 1.252 Å, respectively). For example, the 18h and 6c sites in $Ce_2Co_{15}Mn_3$ and the 8i sites in $CeCo_7Mn_5$ and $CeCo_8Mn_4$ are occupied by the Mn atoms. The majority of the distances $d_{Co\text{-}Co}$ between Co atoms in all analyzed compounds are very close to those between the Co atoms in pure Co metal, namely 2.50 Å. It is to note that in all compounds, except the compound $CeCo_2Mn_{0.33}$, there are positions occupied by Mn atoms for which the distance $d_{Mn\text{-}Mn}$ is smaller that 2.8 Å.

The XPS spectra of the Ce 4d core levels reflect the intermediate valence in $Ce_2Co_{15}Mn_3$, $CeCo_8Mn_4$ and $CeCo_7Mn_5$ compounds. In Fig. 1, the Ce 4d spectrum of $CeCo_8Mn_4$ shows the multiplets arising from the interaction of the 4d hole with the 4f electrons, which are characteristic for all compounds with Ce in the trivalent states (the peaks corresponding to Ce^{3+} are superimposed on the Co 3s peaks at 108.4 and 111.47 eV), and two new peaks at binding energies 118.56 and 122.04 eV. Similar spectrum was observed in $CeCo_7Mn_5$ and $Ce_2Co_{15}Mn_3$ compounds. The last two peaks correspond to the fraction of tetravalent Ce in these three compounds. The spin-orbit splittings are about 3.4 eV for Ce^{3+} and 3.1 for Ce^{4+} in good agreement with the values measured in $CeNi_5$ [6], CeF_4 [7], $CeMn_4Al_8$ and $CeMn_6Al_6$ [19] intermediate valence compounds.

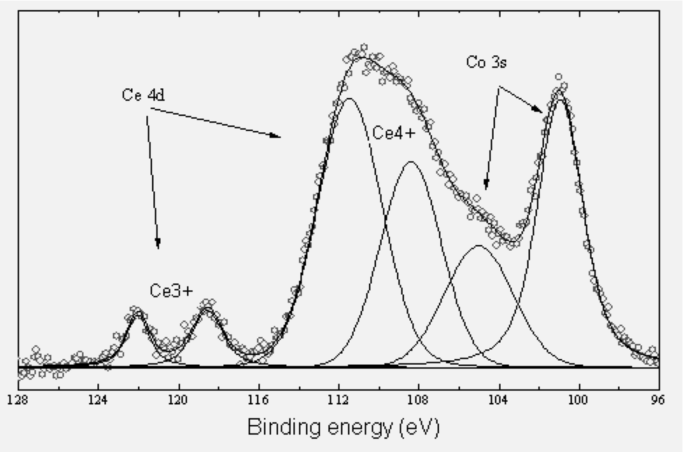

Fig. 1. XPS spectrum of the Ce 4d and Co 3s core levels in $CeCo_8Mn_4$

The exchange interaction J_{dc} between the core hole spin *s* and the 3d electron spin *S* gives rise to a satellite on the high binding energy side of the main line of the Co 3s spectrum [20]. The Co 3s core level spectrum shows an exchange splitting of about 4.2 eV (Fig. 1), which is a direct evidence of the local magnetic moments on Co sites. This value is close to that found in the pure Co metal, namely 4.5 eV [21]. The exchange splitting $\Delta_{ex} = J_{dc}(2S + 1)$ is proportional with the Co local moment $\mu_{Co} = 2S$ [22]. This result suggests that the Co local moment decreases only slightly when going from Co metal to $Ce_2Co_{15}Mn_3$, $CeCo_7Mn_5$ and $CeCo_8Mn_4$.

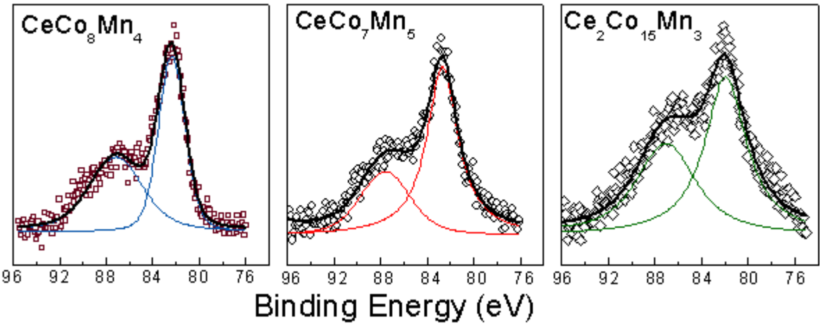

Fig. 2. XPS spectra of Mn 3s in $CeCo_7Mn_5$, $CeCo_8Mn_4$ and $Ce_2Co_{15}Mn_3$

Fig. 2 presents the curve fitting results of Mn 3s spectrum in the $CeCo_8Mn_4$, $CeCo_7Mn_5$ and $Ce_2Co_{15}Mn_3$ compounds, after background subtraction. The Mn 3s core level spectrum shows an exchange splitting around 4.9 eV. Such splittings of about (4–5) eV were observed in the 3s levels of Mn atoms in various intermetallic compounds and alloys, like $Mn_{1-x}Ni_xAl$ [19], $CeMn_4Al_8$ and $CeMn_6Al_6$ [28], $MnPd_{1-x}Sb_x$ [24]. For example, the exchange splitting in MnNi is about 5.2 eV and the Mn magnetic moment is 4 μ_B/Mn[25]. The values obtained for Mn 3s exchange splittings in $Ce_2Co_{15}Mn_3$, $CeCo_8Mn_4$ and $CeCo_7Mn_5$ compounds indicate a mean local magnetic moment per Mn atom of about 3.2 μ_B.

Magnetic field dependences of magnetization at T = 4 and 300 K of $Ce_2Co_{15}Mn_3$ compound are shown in Fig. 3. The saturation magnetizations M_S determined from the extrapolation of magnetization to the zero field are 22.67 μ_B/f.u. at T = 4 K and 18.41 μ_B/f.u. at T = 300 K. The magnetization as a function of temperature for $Ce_2Co_{15}Mn_3$ is shown in the inset of Fig.3.

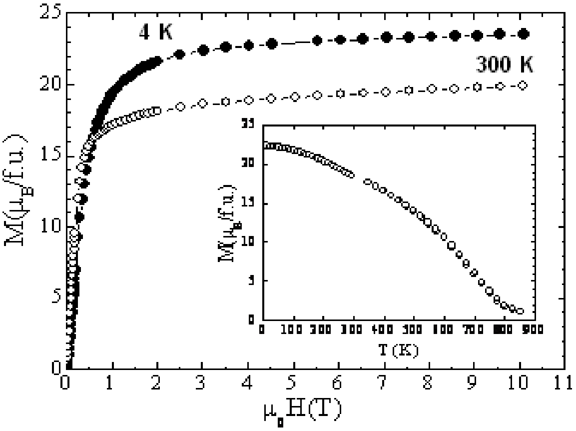

Fig. 3. Magnetization curves of $Ce_2Co_{15}Mn_3$ at 4 and 300 K in magnetic fields up to 10 T. In the inset is shown de temperature dependence of the magnetization

The Curie temperature T_C of $Ce_2Co_{15}Mn_3$ is determined to be 740 K from the temperature dependence of M^2 (T) according to the mean field approach. This value is smaller than the Curie temperature T_C = 772 K found in $Ce_2Co_{15}Mn_2$ compound, which crystallizes in the Th_2Ni_{17} structure type [26]. The values and variations of magnetization of $Ce_2Co_{15}Mn_3$ with field and temperature suggest that this compound has a ferromagnetic behavior below the Curie temperature T_C. The coupling between the Co atoms from different sites is ferromagnetic as usual for Co containing intermetallic, while between the Co and Mn atoms can be expected to be antiferromagnetic. Since the distances between the 18f sites $d_{18f-18f}$ (sites partially occupied by the Mn atoms) in $Ce_2Co_{15}Mn_3$ are smaller than this critical distance, there are some antiferromagnetic Mn–Mn pairs, like in many others Mn based alloys and intermetallic compounds [23, 27]. The antiferromagnetic interactions lead to a decrease of the Curie temperature and of the saturation magnetization per unit formula of $Ce_2Co_{15}Mn_3$ in comparison with values found in Ce_2Co_{17} compound (T_C = 1100 K and M_S = 26.1 μ_B/f.u.) [26]. The competition between these three kinds of interaction Co– Co (the dominant one), Co–Mn and Mn–Mn is expected to lead to a non parallel arrangement of the Mn moments relative to Co moments, which explains the obtained value for the saturation magnetization in $Ce_2Co_{15}Mn_3$.

Although the XPS spectra indicate similar electronic structure of Co and Mn atoms in $CeCo_7Mn_5$ and $CeCo_8Mn_4$, which suggests close values of the local magnetic moments per Co and respectively Mn atoms, the difference in the number of Co and Mn atoms per unit formula leads to very different values of magnetization as a function of magnetic field and temperature.

The magnetic field dependences of magnetizations recorded for temperatures between 5 K and 300 K for $CeCo_7Mn_5$ and $CeCo_8Mn_4$ (in the inset) are shown in Fig. 4 and their temperature dependences in Fig. 5. The values and the variations of magnetizations with field suggest an antiferromagnetic coupling between the transition metal moments located on different sublattices. The dM/dT curve for $CeCo_7Mn_5$ exhibits one local minimum near $T_C \cong 45$ K, ascribed to the ferromagnetic Co - Co coupling and a local maximum near $T_N \cong 150$ K, which can be ascribed to the antiferromagnetic Mn - Mn coupling. The magnetization of $CeCo_8Mn_4$ does not reach saturation even at high fields, but the values of spontaneous magnetization M_{sp} are much higher than those of $CeCo_7Mn_5$. As an example, at 4 K, $M_{sp} = 2.6\ \mu_B$/f.u for $CeCo_8Mn_4$, in comparison with $M_{sp} = 0.7\ \mu_B$/f.u for $CeCo_7Mn_5$. The dM/dT curve for $CeCo_8Mn_4$, shown in the inset of Fig. 5, exhibits one local maximum near $T_N \cong 100$ K and one local minimum near $T_C \cong 173$ K, ascribed like for $CeCo_7Mn_5$ to the antiferromagnetic and ferromagnetic ordering of the 3d magnetic moments. The magnetic susceptibilities for $CeCo_7Mn_5$ and $CeCo_8Mn_4$, measured in the temperature range 300 - 550 K, fit a Curie - Weiss law plus a small additional temperature - independent term with the parameters given in Table 1. From the correlation of the total Curie constants for the two compounds $C = C_{Co} + C_{Mn}$ results the effective magnetic moments per Co and Mn atoms and the values are given in Table 1.

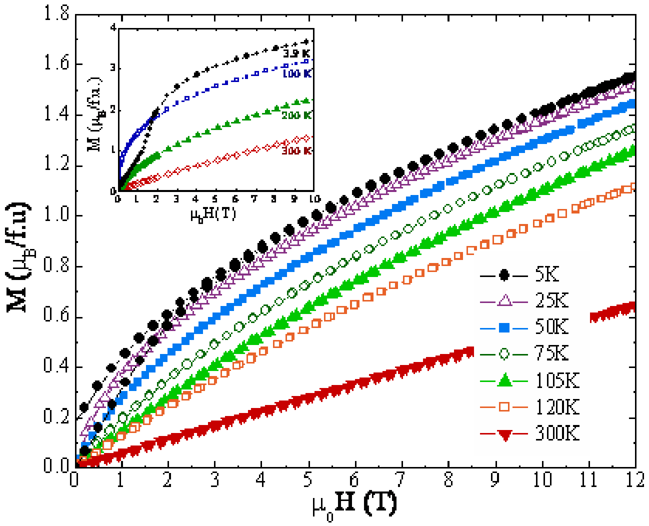

Fig. 4. Magnetization curves of $CeCo_7Mn_5$ and $CeCo_8Mn_4$ (inset) for temperatures between 4 K and 300 K in magnetic field up to 12 T.

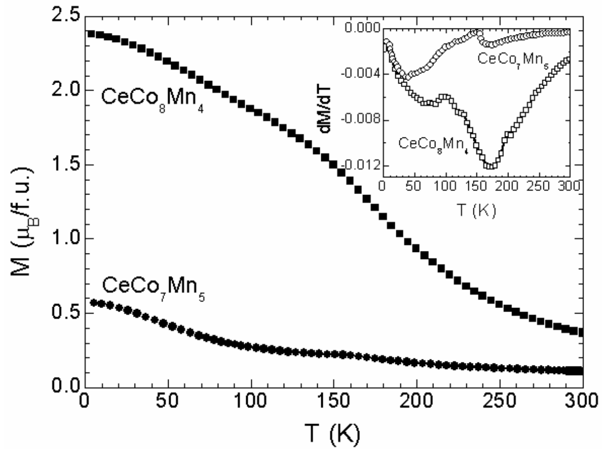

Fig. 5. Temperature dependence of magnetizations for $CeCo_8Mn_4$ and $CeCo_7Mn_5$ in 2 T magnetic field. The inset shows the dM/dT curves.

Table. 1. Magnetic characteristics of the intermetallic compounds from the ternary system Ce-Co-Mn.

Compound	T_C (K)	T_N (K)	μ_{Co} (μ_B)	μ_{Mn} (μ_B)	μ_{eff}^{Co} (μ_B)	μ_{eff}^{Mn} (μ_B)	θ (K)
$Ce_2Co_{15}Mn_3$	740	-	≅1.5	≅ 3.2			
$CeCo_8Mn_4$	173	100	1.6	3.2	2.4	4.08	240
$CeCo_7Mn_5$	45	150	1.6	3.2	2.4	4.08	-175
CeCoMn	-	44	-		-	3.12	-122.1
$CeCoMn_{1.33}$	-	44	-		-	3.22	-183.3
$CeCo_2Mn_{0.33}$	-	-	-	-	-	4.1	-1

Fig. 6 shows the temperature dependence of magnetization for CeCoMn and $CeCoMn_{1.33}$ compounds measured in an applied magnetic fields of 1T and 2T. The M(T) curves exhibit a maximum around 44 K and 35 K, respectively, revealing the antiferromagnetic behavior of the two compounds. Since the Ce and Co atoms do not carry any ordered magnetic moment, like in $CeCo_2$, the magnetic behavior of these alloys is due to the interactions between the Mn local moments. The nearest neighbor Mn-Mn distance between Mn atoms in both alloys is about 2.6 Å, smaller than the critical value, what explains the antiferromagnetic interaction between the neighboring Mn atoms. The upturn of the M(T) curves at lower temperatures is due to traces of magnetic impurities. In contrast with the CeCoMn and $CeCoMn_{1.33}$ compounds, M (T) for $CeCo_2Mn_{0.33}$ reveals the paramagnetic behavior of this compound in the temperature range 5 K - 300 K. The magnetic susceptibility of CeCoMn and

$CeCoMn_{1.}33$ compounds for T> 100 K and of $CeCo_2Mn_{0.33}$ in the measured temperature range may be described with a Curie - Weiss law plus an additional temperature - independent term χ_o, as one can see from the inset of Fig .6, where $1/(\chi - \chi_o)$ is plotted as a function of the temperature. The values of the effective magnetic moments of Mn atoms and of the paramagnetic Curie temperatures are listed in Table 1. The value of the paramagnetic Curie temperature suggests that the interaction between the Mn local magnetic moments in $CeCo_2Mn_{0.33}$ is negligible. This was to be expected due to a larger distance between the Mn moments in comparison with that found in the other two compounds CeCoMn and $CeCoMn_{1.33}$, which are much richer in Mn. In the case of $CeCo_2Mn_{0.33}$ alloy, the Mn atoms are diluted in the $CeCo_2$ matrix and consequently are only expected to be found as second near neighbors.

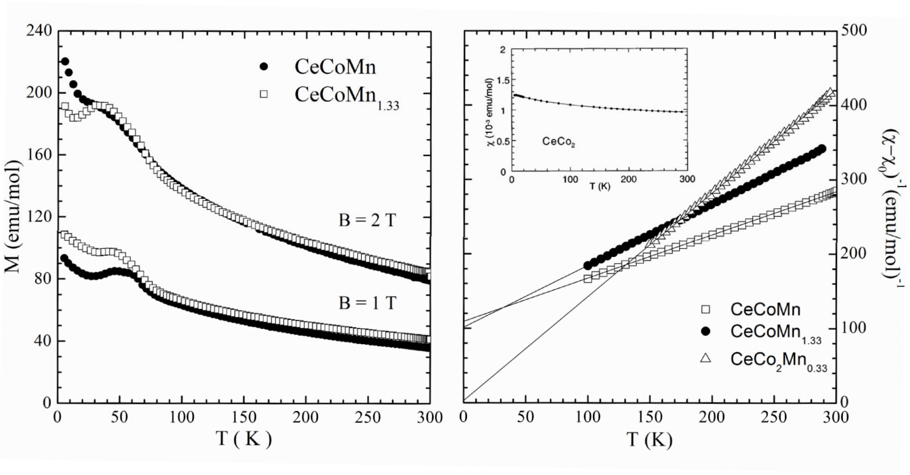

Fig. 6. Temperature dependence of the magnetization for CeCoMn and $CeCoMn_{1.}33$ and the temperature dependence of the reciprocal susceptibilities for CeCoMn, $CeCoMn_{1.}33$ and $CoCo_2Mn_{0.33}$. In the inset is shown the temperature dependence of $CeCo_2$ susceptibility.

CONCLUSIONS

XPS spectra of $Ce_2Co_{15}Mn_3$, $CeCo_7Mn_5$ and $CeCo_8Mn_4$ compounds pointed out the intermediate valence state of Ce ions and that both Co and Mn atoms carry magnetic moments. The complex magnetic structure of these three compounds is determined by the competition between the ferromagnetic (Co-Co pairs) and antiferromagnetic (Co-Mn and Mn-Mn pairs) interactions. The substitution of Co by Mn atoms leads to the decrease of the ferromagnetic interactions and to the increase of the antiferromagnetic interactions.

Both Ce and Co atoms are non-magnetic in CeCoMn, $Ce_3Co_3Mn_4$ and Ce_3Co_6Mn like in the isostructural parent compound $CeCo_2$. Magnetic behavior of these three compounds is mostly due to the Mn moments and depends essentially on the Mn - Mn distances. The interaction between the Mn moments is antiferromagnetic in CeCoMn and $Ce_3Co_3Mn_4$, but a paramagnetic behavior for Ce_3Co_6Mn was evidenced in the studied temperature range.

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