Resonant L$_{\alpha,\beta}$ X-ray emission and L$_3\,2$ X-ray absorption spectra of 3d metals in Co$_2$MnZ (Z = Al, Ga, Sn, Sb) Heusler alloys as an element-selective probe of spin character of valence band

M.V. Yablonskikh$^{a,\ast,c}$, Yu.M. Yarmoshenko$^a$, I.V. Solovyev$^a$, E.Z. Kurmaev$^a$, L.-C. Duda$^b$, T. Schmitt$^b$, M. Magnuson$^b$, J. Nordgren$^b$, A. Moewes$^c$

$^a$ Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 620219 Yekaterinburg, GSP-170, Russia
$^b$ Department of Physics, Uppsala University, Ångström Laboratory, Box 530, 75121 Uppsala, Sweden
$^c$ Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Canada S7N 5E2

Available online 7 March 2005

Abstract

The 3d metal L$_{\alpha,\beta}$ resonant X-ray emission spectra (RXES) and L$_3\,2$ X-ray absorption spectra (XAS) of the Co$_2$MnZ (Z = Al, Ga, Sn, Sb) alloys were measured using linearly polarized soft X-rays. The Mn L$_{\alpha,\beta}$ and Co L$_{\alpha,\beta}$ spectra are compared with results of spin-polarized calculations of Mn 3d and Co 3d partial densities of states performed for each alloy. It is found that a satellite observed at the high-energy side of Mn L$_{\alpha,\beta}$ spectra is due to the localized Mn 3d states located above the Fermi energy. It is shown that the presence of the same satellite structure indicates a higher degree of spin-polarization of Mn 3d states than Co 3d states.

Both the intensity of the satellite structure in Mn L$_{\alpha,\beta}$ spectra and the L$_{\alpha}$/L$_{\beta}$ peak ratio are increased and follow the atomic number of Z element. The effect is especially strong when exciting slightly above the L$_2$ and L$_3$ threshold energies as well as at resonance. We observe a correlation between these spectral parameters and the magnitude of local magnetic moment. The changes occurring in the Mn L$_{\alpha,\beta}$ RXES are in good agreement with a predicted decrease in p–d hybridization (between the atoms of Z element and Mn atoms). The calculated local density of Mn 3d states at the Fermi energy follows the same trend as the hybridization. This suggests that L$_{\alpha,\beta}$ RXES of 3d metals can be used to monitor the degree of spin-polarization of the valence band states and the local density of states at the Fermi level. Note that neither the Mn L$_2\,3$ absorption nor the Co L$_2\,3$ and Co L$_{\alpha,\beta}$ emission spectra of the alloys are affected by the different composition (different Z elements).

© 2005 Elsevier B.V. All rights reserved.

PACS: 78.70 En; 75.25.+z; 75.20.Hr

Keywords: X-ray emission spectra and fluorescence; Local moment in compounds and alloys; Spin arrangements in magnetically ordered materials

1. Introduction

The Mn-based Heusler alloys [1] are ternary intermetallic compounds. These alloys with a composition X$_2$MnZ (L$_2$$_1$ structure), where X is a transition metal and Z belongs to B-subgroup element, have a large magnetic moment which is mostly carried by Mn atoms [2]. It has been found that Co$_2$MnZ alloys, where Z is Si, Al, Ga, Sn, Sb, are ferromagnetic and have relatively large Curie temperatures compared to most other Mn-based Heusler alloys with L$_2$$_1$ structure [3]. Within the framework of exploring the origin of 3d metallic magnetism the interest in their electronic structure and magnetic properties has been renewed [4].

Classic half-metallic ferromagnets, for instance, Co$_2$MnSb [5] or NiMnSb [6] (semi-Heusler alloys with C1b structure) have a density of states (DOS) at the Fermi level (E$_F$) for one of spin projections close or almost equal to zero. According to publications [7,4,3], Co$_2$MnZ alloys have been proposed as almost half-metallic ferromagnets, since they have a relatively small but finite value of DOS for the Mn 3d minority-spin band. For X$_2$MnZ alloys the L$_2$$_1$ structure
is slightly different from Clb, which affects the electronic structure of the Mn atoms [8]. Nevertheless, the influence of the Z atom species affects the minority-spin electrons, making them change their semiconducting character, while the majority-spin electron band remains metallic [9,3]. Recently we have shown that the presence of the energy band gap for Mn 3d minority-spin electrons principally affects the Mn L\textsubscript{2,3}/H\textsubscript{1,2} (3d\textsuperscript{5}/\textsubscript{2}, 3/\textsubscript{2} → 2p\textsubscript{3/2} and 3d\textsuperscript{3}/\textsubscript{2} → 2p\textsubscript{1/2}, respectively) X-ray emission spectra of NiMnSb and Co\textsubscript{2}MnSb, excited by circularly polarized synchrotron radiation [10]. Due to the difference in crystal structure and type of the crystallographic ordering it was not possible to analyze the effects connected to band structure variations by the comparison of the X-ray spectra between these samples. Here, we have used linearly polarized synchrotron radiation to study the changes in the Mn L\textsubscript{2,3}/H\textsubscript{1,2} RXES and L\textsubscript{3} XAS of 3d metals of Co\textsubscript{2}MnZ Heusler alloys as a function of the atomic number of the Z element.

### 2. Experimental setup and calculation details

The samples that we have investigated are polycrystalline. The soft X-ray emission and absorption measurements were performed at beamline 8.0.1 of the advanced light source (ALS) at the Lawrence Berkeley National Laboratory and at beamline IS11-3 of MAX-lab National Laboratory, Sweden. The RXES were acquired using Rowland-circle-type spectrometers with spherical gratings and a multichannel two-dimensional detector [11,12]. The resolution of the spectra was set to approximately 0.9 eV while the resolution of the excitation beam was 0.2 eV. The XAS were measured in the total electron yield mode (TEY) with resolution of 0.1 eV.

Electronic structure calculations in the local-spin-density approximation have been performed using the linear muffin-tin orbital method [13]. The atomic sphere radii for X, Mn and Z were chosen based on the charge neutrality condition inside the spheres and on the experimental lattice parameters, see Table 1. The Brillouin zone integration was performed using the linear tetrahedron method at 172 non-equivalent k-points (corresponding to the 14:14:14 divisions of the reciprocal lattice vectors for the face-centered cubic structure). The calculated DOS’s are given in Fig. 1 for Co\textsubscript{2}MnZ (Z = Al, Ga, Sn, Sb). The minority-spin state DOS’s at the Fermi energy for Mn in Co\textsubscript{2}MnZ nearly vanish. The calculated magnetic moments are found to be in good agreement with the experimental values (Table 1).

### 3. Results and discussion

The 3d metal L\textsubscript{2,3}/H\textsubscript{1,2} RXES of Mn and Co are displayed in Figs. 2 and 3, respectively, along with L\textsubscript{3} XAS. The L\textsubscript{3} XAS of both Co and Mn in Heusler alloys remain almost the same as compared between the alloys. The shape of the Mn L\textsubscript{2,3} spectra and the L\textsubscript{3}/L\textsubscript{2} intensity ratio for L-resonant and off-resonant excitations from (a) to (e) (see in Fig. 2) change with Z atomic number for any of the selected excitation energies. The Co L\textsubscript{2,3}/H\textsubscript{1,2} RXES of the different alloys are almost the same for any selected excitation energy (see in Fig. 3). The observation is in good agreement with previous results obtained using X-ray photoelectron and non-resonant X-ray emission [15]. That difference between the Mn and Co RXES reflects the difference between the Mn 3d and Co 3d DOS’s, which is primarily the stronger spin-polarization of Mn 3d states and their localization above the E\textsubscript{F} (see in Fig. 1) [3]. Large exchange splitting of the Mn 3d electron band leads to the location of minority spin states above the E\textsubscript{F}. In contrast, the Co 3d band possesses metallic character.

**Table 1**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Structure</th>
<th>a (nm)</th>
<th>µ\textsubscript{Mn}</th>
<th>µ\textsubscript{Co}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co\textsubscript{2}MnAl</td>
<td>B2/L\textsubscript{2}</td>
<td>0.5756</td>
<td>3.01/2.847</td>
<td>0.500/0.684</td>
</tr>
<tr>
<td>Co\textsubscript{2}MnGa</td>
<td>L\textsubscript{2}</td>
<td>0.5770</td>
<td>3.02/2.823</td>
<td>0.528/0.687</td>
</tr>
<tr>
<td>Co\textsubscript{2}MnSn</td>
<td>L\textsubscript{2}</td>
<td>0.6000</td>
<td>3.58/3.420</td>
<td>0.758/0.864</td>
</tr>
<tr>
<td>Co\textsubscript{2}MnSb</td>
<td>L\textsubscript{2}</td>
<td>0.9299</td>
<td>3.789/3.552</td>
<td>0.758/0.983</td>
</tr>
</tbody>
</table>

Values of the experimentally determined local magnetic moments were calculated ones are presented for Mn and Co as µ\textsubscript{exp}/µ\textsubscript{calc} in units of µ\textsubscript{B}.

![Fig. 1. Site- and spin-projected state densities of the 3d electrons of Co, Mn and p of Z, where Z is Al, Ga, Sn, Sb, respectively.](image-url)
Fig. 2. Mn $L_{2,3}$ X-ray absorption spectra are shown in the top left frame. The Mn $L_{2,3}$ resonant X-ray emission spectra are displayed in the frames from (a) to (e). The excitation energy indicated by down arrow is the same for every frame and denoted as from (a) to (e) relative to X-ray absorption spectra. The position of the Fermi level $E_F$ is defined from the X-ray photoemission measurements of the same samples [14], where it corresponds to the Mn 2p core level binding energy.

From the changes in the intensity distribution of the Mn $L_{2,3}$ spectra of Co$_2$MnZ with variations in the atomic number of element Z we can monitor the evolution of the Mn 3d DOS between the different alloys. Although the spin-polarization of Mn 3d band remains almost the same for each substitution of the Z element, see Fig. 1, the structure of the Mn 3d DOS may significantly vary due to p–d hybridization between the electrons of Z element and Mn [19]. According to calculations [19, 3], change of the type and concentration of Z element may result in the formation of a semiconducting band.

Fig. 3. The Co $L_{2,3}$ XAS and Co $L_{2,3}$ RXES. All designations are similar to used in Fig. 2. The position of the Fermi level $E_F$ is defined from the X-ray photoemission measurements of the same samples [15], where it corresponds to the Co 2p$_{3/2}$ core level binding energy.
Hence, the 2p minority-spin electron excited above the selection rules, in contrast to the situation for Co RXES, hole of minority spin due to spin-selectivity of the dipole moment decay. There are almost no minority-spin electrons in minority-spin states followed by its relaxation via fluorescence of the excited 2p electron to be trapped in the Mn 3d band below the L3 threshold, see Fig. 2 (c) and (d) and the intensity with the following observations. First, the estimated distance between the two peak maxima for Mn L3 RXES of (a) and (b) in Fig. 2 is approximately 3–4 eV which is similar to the formation of Mn L3 RXES between Co and Mn only RXES excited with the energy at and above the L3 absorption, the relaxation of the 2p3/2 core level binding energy in the emission energy scale, and no double structure is detected for Co L3 RXES obtained at L1 and above L3 resonant excitation. For Mn L3 RXES excited with the energy at and above the L3 absorption, the relaxation of the 2p3/2 intermediate state is affected by the high probability of the excited 2p electron to be trapped in the Mn 3d minority-spin states followed by its relaxation via fluorescent decay. There are almost no minority-spin electrons in the occupied part of the Mn 3d band to refill the 2p core hole of minority spin due to spin-selectivity of the dipole selection rules, in contrast to the situation for Co RXES. Hence, the 2p minority-spin electron excited above the L3 RXES is trapped in the localized Mn d states [3] having limited possibility of non-fluorescent d–d relaxation to the occupied part of the band due to the small DOS near the EF. Consequently, the 2p core holes with appropriate spin are refilled not only by the d electrons of majority spin from the band below the EF, but also from the Mn 3d minority-spin states above the nominal EF which were populated due to the excitation process. The latter assumption agrees well with the following observations. First, the estimated distance between the two peak maxima for Mn L3 RXES spectra (a) and (b) in Fig. 2 is approximately 3–4 eV which is similar to the formation of Mn L3 RXES between Co and Mn only RXES of Co3MnSb alloys using circularly polarized light where the largest dichroism was observed at the high energy side of the Mn L3 RXES around the photon energy 640.5 eV taken at L3 and off L3 resonance [10]. The similar effects describing the prominent behavior of Cr as compared to metallic reference have been also observed for half-metallic CrO2 [22].

4. Conclusion

The 3d metal L3,2 RXES are found to be useful for monitoring the changes in the 3d band and for qualitative indication of the degree of strong spin-polarization of metal d states in metallic Heusler alloys. The Mn L3,2 RXES of Co3MnZ vary according to the Z atomic number. These changes can be largely attributed to corresponding variations of the Mn 3d DOS character of the valence band. Neither the linearly polarized Mn L3,3 XAS nor the Co L2,3 XAS do not reveal this kind of information.

Acknowledgments

Support from the Royal Swedish Academy of Sciences for cooperation between Sweden and the former Soviet Union is gratefully acknowledged. The Uppsala group gratefully acknowledges financial support from the Swedish Research Council (VR) and the Göran Gustafsson Foundation. Funding by the Saskatchewan Synchrotron Institute and the Natural Sciences and Engineering Research Council of Canada (NSERC) are gratefully acknowledged. A. Moewes is a Canada Research Chair. The help of the staffs of beamline 8.0.1 (ALS) and I511-3(MAX-lab) is greatly appreciated.

References