J. Elec. Spec. Related Phen. **144–147**, 765–769 (2015)

Resonant $L_{\alpha,\beta}$ X-ray emission and $L_{3,2}$ X-ray absorption spectra of 3d metals in Co_2MnZ (Z = Al, Ga, Sn, Sb) Heusler alloys as an element-selective probe of spin character of valence band

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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_2MnZ (Z = Al, Ga, Sn, Sb) alloys were measured using linearly polarized soft X-rays. The Mn L_α and Co L_α 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_a 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_α spectra and the L_β/L_α, peak ratio are increased and follow the atomic number of Z element. The effect is especially strong when excitating slightly above the L_3 and L_2 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).

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_2MnZ ($L2_1$ 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_2MnZ 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 $L2_1$ 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, CoMnSb [5] or NiMnSb [6] (semi-Heusler alloys with $C1_b$ structure) have a density of states (DOS) at the Fermi level (E_F) for one of spin projections close or almost equal to zero. Ac- cording to publications [7,4,3], Co_2MnZ 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_2MnZ alloys the $L2_1$ structure

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doi:10.1016/j.elspec.2005.01.064

is slightly different from $C1_b$, 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_α, L_β ($3d_{5/2,3/2}$ –> $2p_{3/2}$ and $3d_{3/2}$ –> $2p_{1/2}$, respectively) X-ray emission spectra of NiMnSb and Co_2MnSb, excited by circularly polarized synchrotron radiation [10].

Table 1: Structural and magnetic parameters of the investigated Heusler alloys (extracted from [2])

Alloy	Structure	a (nm)	μ_{Mn}	μ_{Co}
Co_2MnAl	$B2/L2_1$	0.5756	3.01/2.847	0.50/0.684
Co_2MnGa	$L2_1$	0.5770	3.01/2.923	0.52/0.687
Co_2MnSn	$L2_1$	0.6000	3.58/3.420	0.75/0.864
Co_2MnSb	$L2_1$	0.5929	3.79/3.552	0.75/0.983

Values of the experimentally determined local magnetic moments via calculated ones are presented for Mn and Co as μ_{exp}/μ_{calc} in units of μ_B.

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 $L_{\alpha,\beta}$ RXES and $L_{2,3}$ XAS of 3d metals of Co_2MnZ 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 I511-3 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_2MnZ (Z = Al, Ga, Sn, Sb). The minority-spin state DOS's at the Fermi energy for Mn in Co_2MnZ 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 $L_{\alpha,\beta}$ RXES of Mn and Co are displayed in Figs. 2 and 3, respectively, along with $L_{3,2}$ XAS. The $L_{3,2}$ XAS of both Co and Mn in Heusler alloys remain almost the same as compared between the alloys. The shape of the Mn L_α spectra and the L_β/L_α 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 $L_{\alpha,\beta}$ 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_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_F. In contrast, the Co 3d band possesses metallic character

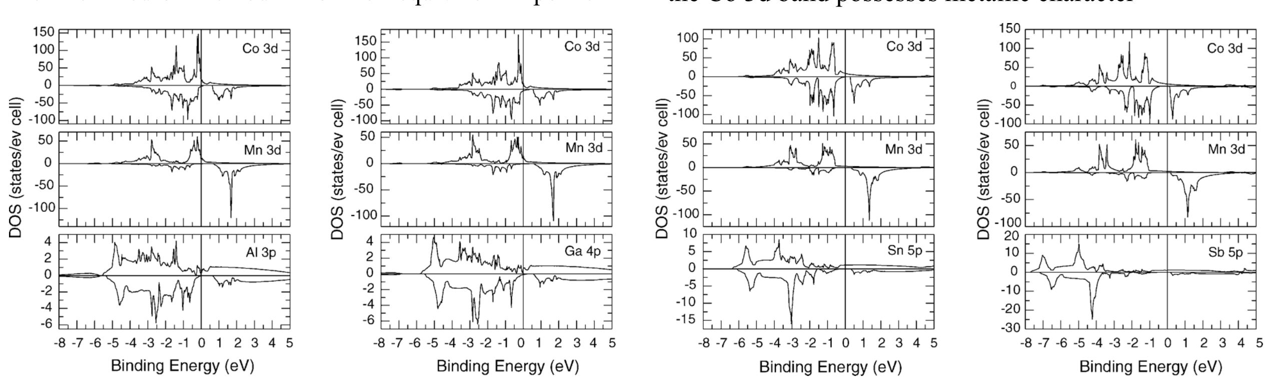

Fig. 1: Site- and spin-projected state densities of the 3d electrons of Co, Mn and p of Z, where Z is Al, Ga, Sn, Sb, respectively.

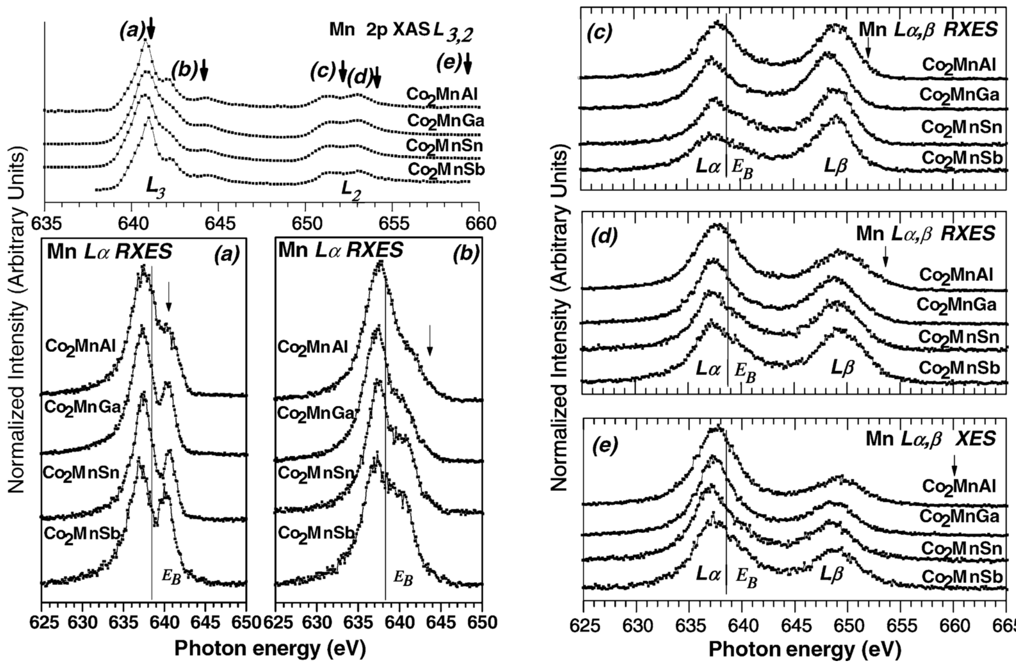

Fig. 2: Mn $L_{2,3}$ X-ray absorption spectra are shown in the top left frame. The Mn $L_{\alpha,\beta}$ resonant X-ray emission spectra are displayed in the frames from (a) to (e). The excitation energy indicated by down arrow is the same for every frame and denoted as from (a) to (e) relative to X-ray absorption spectra. The position of the Fermi level E_B is defined from the X-ray photoemission measurements of the same samples [14], where it corresponds to the Mn $2p_{3/2}$ core level binding energy.

From the changes in the intensity distribution of the Mn L_α spectra of Co_2MnZ 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 gap.

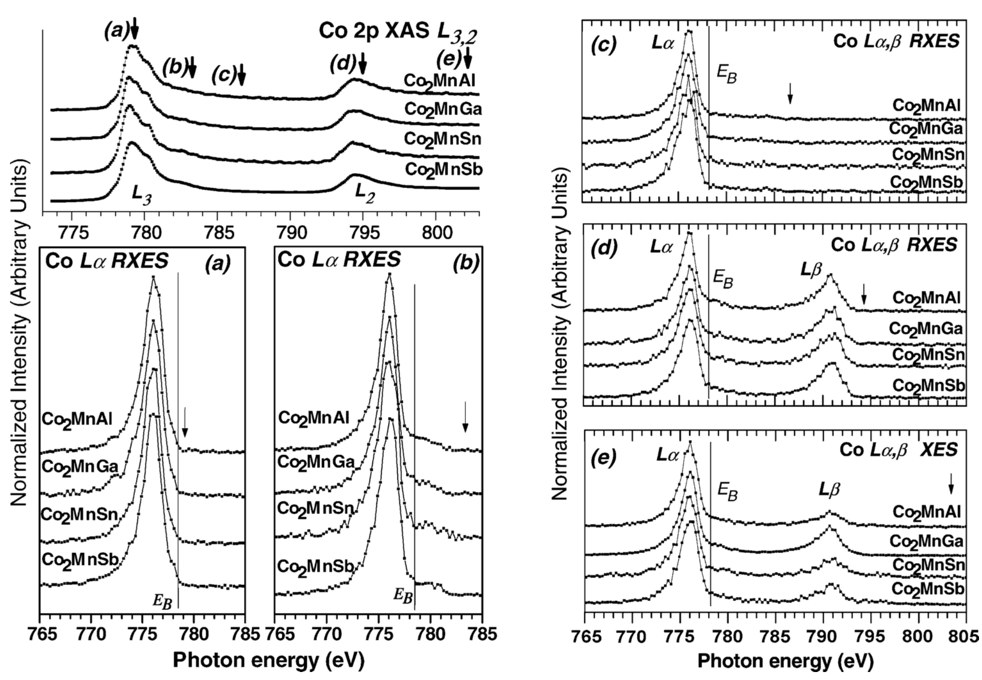

Fig. 3: The Co $L_{2,3}$ XAS and Co $L_{\alpha,1}$ RXES. All designations are similar to used in Fig. 2. The position of the Fermi level E_B is defined from the X-ray photoemission measurements of the same samples [15], where it corresponds to the Co $2p_{3/2}$ core level binding energy.

In agreement to present calculation, the spin-polarization is also slightly changed following the Z atomic number [4]. The latter predictions are found to be in good agreement with present experimental results.

Both the peak ratio L_β/L_α acquired for excitations above the L_2 threshold, see Fig. 2(c) and (d) and the intensity of the satellite structure at the high-energy side of Mn L_α RXES excited at L_3 but below the L_2 resonance, see Fig. 2(a) and (b) are increased following the Z as compared to similar data of Co RXES. An increase of the atomic number of the Z-element correlates with the lattice parameter a and with the local magnetic moment of Mn, which is in good agreement with experimental neutron scattering results [18,16,17] (see Table 1). Consequently, these spectral features are considered as a characteristic of Mn 3d magnetic moment and may depend on the spin-polarization of the d shell as well as the magnitude of the local magnetic moment [21].

We recall that the $L_{\alpha,\beta}$ X-ray emission reflects 3d DOS only indirectly due to the complexity of the photon scattering process, as seen, for example in the Mn $L_{\alpha,\beta}$ RXES of Ni–Mn alloys [20]. For the sake of simplicity, we will com- pare the formation of L_α RXES between Co and Mn only qualitatively considering the fluorescent relaxation from the intermediate to the final state. For the case of Co L_α RXES formation, the $2p_{3/2}$ core hole with any spin will be refilled by radiative transition of Co d electron from the occupied part of the band since majority and minority-spin states are located below the E_F. Consequently, the Co L_α spectrum is located below the Co $2p_{3/2}$ core level binding energy in the emission energy scale, and no double structure is detected for Co L_α RXES obtained at L_3 and above L_3 resonant excitation. For Mn L_α RXES excited with the energy at and above the L_3 absorption, the relaxation of the $2p^5 3d^{n+1}$ 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 E_F is trapped in the localized Mn d states [3] having limited possibility of non-fluorescent d–d relaxation to the occu- pied part of the band due to the small DOS near the E_F. Consequently, the 2p core holes with appropriate spin are refilled not only by the d electrons of majority spin from the band below the E_F, but also from the Mn 3d minority-spin states above the nominal E_F 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 L_a spectra (a) and (b) in Fig. 2 is approximately 3–4 eV which is similar to taken from the Mn 3d band calculations between the maxima of majority-spin DOS and the maxima of minority-spin Mn 3d DOS (see Fig. 1). Second, the Mn L_α RXES enhances to the photon energies above the Mn $2p_{3/2}$ core level binding energy which is contrary to the situation with Co L_α RXES. Further, the assumption is in good agreement with the approach describing the formation of Mn L_α RXES for Co_2MnSb alloys using circularly polarized light where the largest dichroism was observed at the high energy side of the Mn L_α RXES around the photon energy 640.5 eV taken at L_3 and off L_3 resonance [10]. The similar effects describing the prominent behavior of Cr as compared to metallic reference have been also observed for half-metallic CrO_2 [22].

4. Conclusion

The 3d metal $L_{\alpha,\beta}$ 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 $L_{\alpha,\beta}$ RXES of Co_2MnZ 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 $L_{2,3}$ XAS nor the Co $L_{2,3}$ 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

[1] F. Heusler, Verh. Dtsch. Phys. Ges. 5 (1903) 219.
[2] P.J. Webster, K.R.A. Ziebeck, Alloys and Compounds of d-Elements with Main Group Elements, Part 2, Landolt-Boo¨rnstein Edition, vol. 19, New Series, Group III Springer-Verlag, Berlin, 1988, pp. 75–184, and references therein.
[3] J. Kübler, A.R. Williams, C.B. Sommers, Phys. Rev. B 28 (1983) 1745.
[4] S. Picozzi, A. Continenza, A.J. Freeman, Phys. Rev. B 66 (2002) 094421 and references therein.
[5] J. Kübler, Physica B+C 127 (1984) 257.
[6] R.A. de Groot, F.M. Mueller, P.G. Vanengen, K.H.J. Buschow, Phys. Rev. Lett. 50 (1983) 2024.
[7] P.J. Brown, K.U. Neumann, P.J. Webster, K.R.A. Ziebeck, J. Phys.: Condens. Matter. 12 (2000) 1827.
[8] V.Yu. Irkhin, M.I. Katsnelson, Uspekhi Fiz. Nauk 164 (1994) 705 [Engl. transl.: Phys. Uspekhi 37 (1994) 659].

[9] S. Ishida, S. Fujii, S. Kawhiwagi, S. Asano, J. Phys. Soc. Jpn. 64 (1995) 2152.
[10] M.V. Yablonskikh, Y.M. Yarmoshenko, V.I. Grebennikov, E.Z. Kurmaev, S.M. Butorin, L.C. Duda, J. Nordgren, S. Plogmann, M. Neumann, Phys. Rev. B 63 (2001) 235117.
[11] J.J. Jia, T.A. Callcott, J. Yurkas, A.W. Ellis, F.J. Himpsel, M.G. Samant, J. Stohr, D.L. Ederer, J.A. Carlisle, E.A. Hudson, L.J. Terminello, D.K. Shuh, R.C.C. Perera, Rev. Sci. Instrum. 66 (1995) 1394.
[12] J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J.E. Rubensson, N. Wassdahl, Rev. Sci. Instrum. 60 (1989) 1690.
[13] O.K. Andersen, Phys. Rev. B 12 (8) (1975) 3060.
[14] S. Plogmann, T. Schlatholter, J. Braun, M. Neumann, Y.M. Yarmoshenko, M.V. Yablonskikh, E.I. Shreder, E.Z. Kurmaev, A. Wrona, A. Slebarski, Phys. Rev. B 60 (1999) 6428.
[15] M.V. Yablonskikh, Y.M. Yarmoshenko, E.G. Gerasimov, V.S. Gaviko, M.A. Korotin, E.Z. Kurmaev, S. Bartkowski, M. Neumann, J. Magn. Magn. Mater. 256 (2003) 396.
[16] K.R.A. Ziebeck, P.J. Webster, J. Phys. Chem. Solids 35 (1) (1974) 1.
[17] P.J. Webster, Cont. Phys. 10 (6) (1969) 559–565.
[18] P.J. Webster, M.R.I. Ramadan, J. Magn. Magn. Mater. 5 (1977) 51.
[19] S. Fujii, S. Ishida, S. Asano, J. Phys. Soc. Jpn. 64 (1995) 185.
[20] F. Borgatti, P. Ferriani, G. Ghringhelli, A. Tagliaferri, B. De Michelis, C.M. Bertoni, N.B. Brookes, L. Braicovich, Phys. Rev. B 65 (9) (2002) 94406.
[21] J. Badro, G. Fiquet, F. Guyot, J.P. Rueff, V.V. Struzhkin, G. Vanko, G. Monaco, Science 300 (5620) (2003) 789.
[22] E.Z. Kurmaev, A. Moewes, S.M. Butorin, M.I. Katsnelson, L.D. Finkelstein, J. Nordgren, P.M. Tedrow, Phys. Rev. B 67 (2003) 155105.