

State of Co and Mn in half-metallic ferromagnet Co_2MnSi explored by magnetic circular dichroism in hard X-ray photoelectron emission and soft X-ray absorption spectroscopies

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The half-metallic Heusler compound Co_2MnSi is a very attractive material for spintronic devices because it exhibits very high tunnelling magnetoresistance ratios. This work reports on a spectroscopic investigation of thin Co_2MnSi films as they are used as electrodes in magnetic tunnel junctions. The investigated films exhibit a remanent in-plane magnetisation with a magnetic moment of about $5 \mu_B$ when saturated, as expected. The low coercive field of only 4 mT indicates soft magnetic behaviour. Magnetic dichroism in emission and absorption was measured at the Co and Mn $2p$ core levels. The photoelectron spectra were excited by circularly polarised hard X-rays with an energy of 6 keV and taken from the remanently magnetised film. The soft X-ray absorption spectra were taken in an induction field of 4 T. Both methods yielded large dichroism effects. An analysis reveals the localised character of the electrons and magnetic moments attributed to the Mn atoms, whereas the electrons related to the Co atoms contribute an itinerant part to the total magnetic moment.

Keywords: Half-metallic ferromagnets, Heusler compounds, Thin films, Magnetic dichroism, Photoelectron spectroscopy, Photoabsorption spectroscopy, XMCD, Electronic structure.

1. Introduction

Half-metallic ferromagnets (HMFs) have attracted increasing interest because of their possible ap-

plications in spintronics devices. Their use has been suggested to realise spin-dependent devices such as spin injectors, tunnelling magnetoresistance (TMR) junctions, and giant magnetoresistance devices. In HMF materials, the minority spin density of states (DOS) exhibits a band gap at the Fermi energy ϵ_F , while the majority spins are responsible for the metallic properties. Among them, Co₂-based Heusler alloys with $L2_1$ structure [prototype Cu₂MnAl, cF16, space group $Fm\bar{3}m$ (225)] have attracted attention for future application as ferromagnetic electrodes in spintronic devices [1]. In particular, Co₂MnSi, with a high Curie temperature of 985 K and large magnetic moment of $5 \mu_B$, has been explored over a long period [2–5]. Very recently, the half-metallicity of Co₂MnSi thin films was directly reported. A spin polarisation of 93% at room temperature was measured by *in-situ* spin-resolved ultraviolet photoelectron spectroscopy [6]. Several groups developed fully epitaxial magnetic tunnel junctions (MTJs) based on Co₂MnSi as a lower electrode and an AlO_x [7,8] or MgO [9,10] tunnelling barrier. The TMR ratio of Co₂MnSi-based MTJs was improved from 570% [8] to 1135% [11] at 4.2 K. Systematic studies of the effect of nonstoichiometry on the spin-dependent tunnelling characteristics of Co₂Mn _{α} Si-based MTJs have shown a direct dependence of the TMR ratio on the Mn content α . Recently, giant TMR ratios of up to 1995% at 4.2 K and up to 354% at 290 K were obtained for epitaxial off-stoichiometric Co₂Mn_{1.35}Si_{0.88}/MgO/Co₂Mn_{1.35}Si_{0.88} MTJs [12]. It is incontrovertible that the Mn content influences the TMR ratio in Co₂MnSi-based MTJs. To understand the Mn behaviour in this type of Heusler compound, more element-specific investigation is required.

Since the observation of X-ray magnetic circular dichroism (XMCD) from Fe with hard X-rays (K edge) by Schütz *et al.* [13] and of Ni with soft X-rays (L edges) by Chen [14], XMCD measurements are widely used as a variant of X-ray absorption spectroscopy (XAS) to investigate the magnetic properties of complex systems in an element-specific way. XMCD enables the determination of the magnetic properties of the constituent elements of materials, as well as their spin and orbital magnetic moments, using integral sum rules [15]. XMCD investigation of several Heusler compounds and thin films verified the localised character of the Mn $3d$ valence states [16,17]. The $L_{3,2}$ edge absorption spectra for

left and right circularly polarised soft X-rays reflect the spin-resolved partial density of states (PDOS) at the $3d$ transition metal atoms. XMCD studies of epitaxial Heusler thin films of Co₂Mn_{1- x} Fe _{x} Si provided a pathway for the improvement of HMF materials and interfaces for spintronic devices using a calculation scheme for recovering the spin-resolved unoccupied Co DOS [18]. In contrast to photon absorption, photoelectron spectroscopy allows a detailed illustration of the occupied states (valence band) close to the Fermi energy.

Hard X-ray photoelectron spectroscopy (HAXPES) has evolved into the most relevant, powerful, and nondestructive method of investigating the bulk electronic structure of solids, thin films, and multilayers. Owing to the large electron escape depth (the electron mean free path at kinetic energies of 6 keV is about 17 nm), it was possible to detect the valence band of buried Co₂MnSi Heusler compounds underneath 20 nm MgO, which was comparable with those of the bulk material [19,20]. The combination of HAXPES with variable photon polarisation provides, in addition to the electronic structure, the magnetic structures of buried layers. Very recently, magnetic circular dichroism in the angular distribution of photoelectrons (MCDAD) from core states provided another hint regarding the localised character of the magnetic moments of some transition elements, such as Fe and Co [21]. In FeGd, MCDAD of the rare earth element Gd reflects a stronger temperature dependence of the Gd moment compared to that of Fe [22].

The present study reports on a detailed investigation of the magnetic structure of epitaxial Co₂MnSi thin films. The spin-resolved DOSs are calculated using full potential *ab-initio* methods. Circularly polarised radiation in combination with bulk-sensitive HAXPES is used to study the magnetic circular dichroism of the core states. The element-specific magnetic moments are investigated by circular dichroism in XAS.

2. Experimental details

Half of a stack for MTJs was prepared by DC/RF sputtering with 4" magnetrons. The layers were deposited on MgO substrates in the following order: MgO(001)/MgO{5}/Co₂MnSi{20}/MgO{2}. The numbers in braces give the thickness of the layers in nm. A 5 nm thick MgO layer was deposited onto the MgO(001) substrate to level out defects of its surface. This results in an improved structure of

the Heusler layer. All the layers of the films were deposited at room temperature. The argon process pressure was set to 1.5×10^{-3} mbar in the sputtering system, where the base pressure was about 10^{-7} mbar. The samples were post-annealed for 1 h at 400°C in vacuum (2×10^{-7} mbar).

The magnetic properties of the films were determined at room temperature using an alternating-gradient magnetometer. The films exhibit an in-plane magnetic anisotropy. The measured hysteresis loop is shown in Figure 1. The saturation moment is $5 \mu_B$, as expected. The films are rather soft magnetic with a coercive field of only 4 mT. The magnetic moment in remanence is $2.4 \mu_B$, which is about half of the saturation moment.

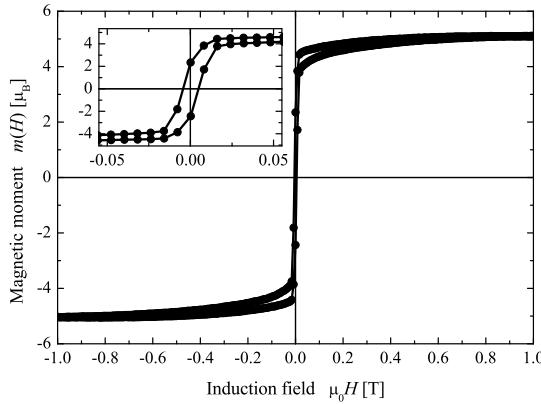


Fig. 1. Magnetisation of Co_2MnSi thin films. The hysteresis was measured at room temperature using an alternating-gradient magnetometer.

The HAXPES measurements were made at beamline P09 [23] of PETRA III (Hamburg). See Reference [24] for the details of the HAXPES setup. The photon energy was set to $h\nu = 5947.9$ eV using a Si(111) high heat load double-crystal primary monochromator and the (333) reflection of a Si double channel-cut post monochromator. The resolution of the monochromator is better than 100 meV. The magnetic circular dichroism was measured at a fixed magnetisation by changing the helicity of the photons. The thin films were magnetised *in situ* along the direction of the photon beam after they were introduced into the ultrahigh-vacuum (UHV) μ -metal chamber. The helicity of the photons was changed using the (111) reflection of an in-vacuum phase retarder based on a $400 \mu\text{m}$ thick diamond single crystal with (100) orientation [25]. The degree of circular polarisation is about 98 to 99%. The energy in the spectra is given with respect to the Fermi

energy ϵ_F , which was calibrated from measurements of a Au sample. ϵ_F appeared at a kinetic energy of $E_{kin} = 5946.48$ eV with a width of 200 meV. Accounting for the 28 meV thermal broadening of the Fermi-Dirac distribution at room temperature (300 K), this corresponds to an overall energy resolution of about 170 meV ($E/\Delta E \approx 3.5 \times 10^4$). The setup of the HAXPES-MCDAD experiment is sketched in Figure 2. A retractable Fe-Nd-B permanent magnet was used to magnetise the sample remanently or change the direction of magnetisation. It supplies an induction field of about ± 1 T, which is high enough to saturate the magnetisation of the thin film (compare Figure 1).

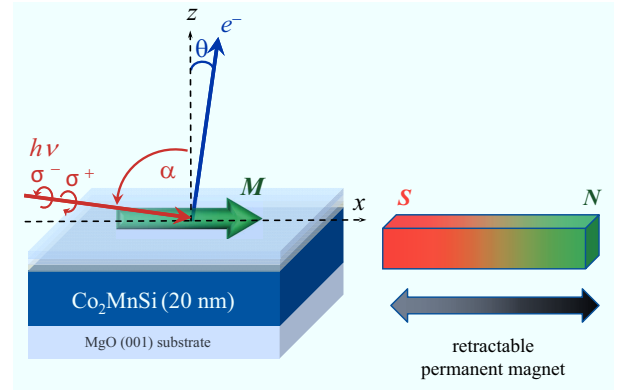


Fig. 2. (Color online) HAXPES setup for MCDAD measurements of Co_2MnSi thin films.

The remanent magnetisation M is changed *in situ* by a retractable Fe-Nd-B permanent magnet supplying an induction field of about ± 1 T. The measurements are performed with circularly polarised photons of opposite helicity (σ^+ or σ^-) that impinge on the sample with an angle of incidence of $\alpha = 89^\circ$. The electrons are detected in a near-normal emission geometry with $\theta = 1^\circ$ and an angular resolution of about $\Delta\theta \pm 15^\circ$.

The X-ray absorption spectroscopy and X-ray magnetic circular dichroism experiments were performed at the undulator beamline ID08 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The measurements were performed in a UHV chamber with a pressure in the low 10^{-10} mbar range at room temperature. XAS was conducted at the Mn and Co $L_{3,2}$ edges in the energy ranges of 625 to 685 eV and 765 to 835 eV, respectively. The energy resolution of the *Dragon*-type monochromator was set to about 250 meV ($E/\Delta E > 2.5 \times 10^3$). The degree of circular polarisation delivered by the *Apple II*-type undulator is larger than 99%. A rapidly switchable high-field magnet was used to obtain the XMCD signal. The induction field was fixed at $\mu_0 H = 4$ T and ensures

saturation in the out-of-plane geometry. Measurements were performed for a *normal* geometry with the photon beam parallel to the surface normal and for a *grazing* geometry with an angle of incidence of $\theta = 70^\circ$. The magnetic field direction was chosen parallel to the incident photon beam in both cases. The setup of the XMCD experiment is sketched in Figure 3.

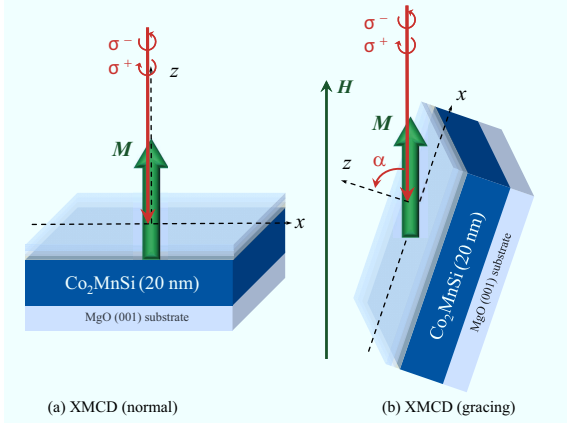


Fig. 3. (Color online) X-ray absorption setup for XMCD experiments on Co_2MnSi thin films.

The magnetisation M is induced by a magnetic field H applied during the measurement with circularly polarised photons of opposite helicity (σ^+ or σ^-). Note that H and M are generally parallel only in isotropic, soft magnetic materials.

3. Results and discussion

3.1. Electronic structure of Co_2MnSi

The electronic structure was calculated using the full-potential linear augmented plane wave (FPLAPW) method as implemented in WIEN2k [26, 27]. The details of the calculations are reported in References [28, 29]. The atoms were placed on the 8c (Co), 4b (Mn), and 4a (Si) Wyckoff positions of the $L2_1$ structure with space group $Fm\bar{3}m$ (225). The charge density and other site-specific properties were analysed using Baader's quantum theory of atoms in molecules (QTAIM) [30] using the built-in routines of WIEN2k as well as the CRITIC2 package of the programs [31, 32].

Figure 4 shows the result of the electronic structure calculations. The compound exhibits a DOS that is typical of HMFs. The minority density has a band gap at the Fermi energy. A closer inspection reveals that the size of the band gap is determined by states attributed to the Co atoms. The minority gap has a width of $\Delta E = 0.82$ eV. The top of the

minority valence band is about 0.32 eV below ϵ_F . Owing to the half-metallic character, the magnetic moment in the primitive cell is $5 \mu_B$, as expected from the Slater–Pauling rule [33].

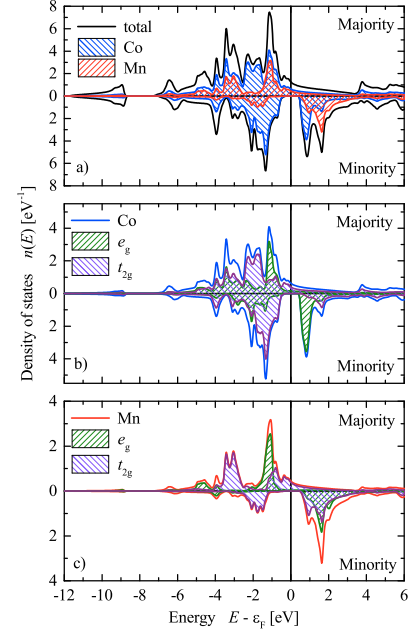


Fig. 4. (Color online) Electronic structure of Co_2MnSi . (a) Total DOS, (b) Co PDOS, (c) Mn PDOS.

Figure 5 shows the valence charge density $\rho(\mathbf{r})$ and the magnetisation density $\sigma(\mathbf{r})$ in the (110) plane of Co_2MnSi . The magnetisation density $\sigma(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) - \rho_\downarrow(\mathbf{r})$ is calculated from the difference of the spin densities arising from majority ($\uparrow$) and minority ($\downarrow$) valence electrons, whereas the valence charge density is calculated from the sum $\rho(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r})$. The magnetisation density is higher at the Mn atoms compared to the Co atoms and vanishes at the Si atoms, as expected. Baader's QTAIM analysis was used to analyse the charge density and magnetic moments. The results of the QTAIM analysis are listed in Table 3.1. A small charge transfer is observed. On average, about 0.3 electrons are transferred from the Mn and Si atoms to the Co atoms.

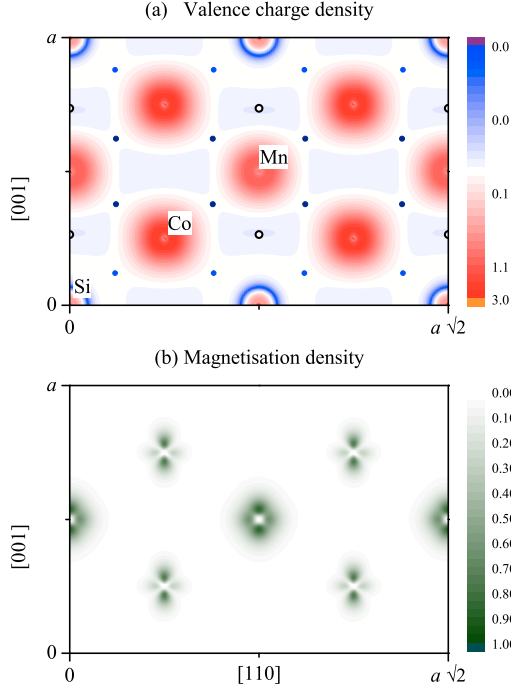


Fig. 5. (Color online) Charge and spin density of Co_2MnSi . Shown are the valence charge density (a) and the magnetisation density (b) in the (110) plane. Mn is in the centre of the cell, and Si is located at (0,0). The bond and cage critical points are marked by closed and open symbols, respectively (see also Table 3.1 for the positions). Note the logarithmic colour scale of the charge density. Both densities are given in atomic units.

Table 1. QTAIM analysis of Co_2MnSi .

V are the basin volumes V , n_e is the number of electrons in the basin, and $q = Z - n_e$ is the electron excess/deficiency with respect to the electron occupation in free atoms Z . Negative values indicate electron excess, that is, negatively charged ions. m is the magnetic moment in the basin in multiples of the Bohr magneton.

	$V [\text{\AA}^3]$	n_e	q	$m [\mu_B]$
Co	11.525	27.345	-0.345	1.064
Mn	9.975	24.467	0.533	2.972
Si	11.909	13.841	0.159	-0.028

The topology of the charge density $\rho(\mathbf{r})$ is characterised by critical points where $\rho(\mathbf{r})$ has an extremal value, that is for $\nabla\rho(\mathbf{r}) = 0$. Besides the gradient $\nabla\rho(\mathbf{r})$, the extrema or critical points of $\rho(\mathbf{r})$ are also characterised by the Laplacian $\nabla^2\rho(\mathbf{r})$. Four different types of critical points $(\mathbf{r}, \mathbf{s})$ exist in

solids that are classified by their rank $\mathbf{r}$ and signature $\mathbf{s}$:

- **(3,-3)** are local maxima of $\rho(\mathbf{r})$. These points appear at the position of an atom and are called *nuclear* critical points.
- **(3,-1)** are saddle points with a local minimum of $\rho(\mathbf{r})$ in 1 direction of space and a maximum in the other two. These points appear on the line between two neighbouring atoms and thus define the bond between them. Therefore, they are called *bond* critical points.
- **(3,+1)** are also saddle points but with a maximum in one and a minimum in the other two directions of space. These are called *ring* critical points because they appear in the middle of several bonds forming a ring.
- **(3,+3)** are local minima of $\rho(\mathbf{r})$ and called *cage* critical point.
- **(0, 0)** is a critical point at infinity that appears only in molecules but not in solids.

The QTAIM critical points of Co_2MnSi and their properties are summarised in Table 3.1. There are, indeed, three different nuclei that act as attractors. A cage critical point c is found between Mn and Si along the [001] axis and acts as a repeller. It is an absolute minimum of the charge density. Further, two bond critical points $b_{1,2}$ are found; they are located between Co and Si (b_1) and between Co and Mn (b_2). When the two ring critical points $r_{1,2}$ are also considered, the Morse invariant relationships: $n_n > 1, n_b > 3, n_r > 3, n_c > 1$ are fulfilled and the Morse sum of the numbers n_i of the different critical points vanishes ($n_n - n_b + n_r - n_s = 0$) [34], as expected for crystals. The latter is also known as the Euler or the Poincaré–Hopf relation.

Table 2. QTAIM critical point analysis of Co_2MnSi .

pg is the point group symmetry of the critical point, and W is the Wyckoff position including the multiplicity of the critical points in the full cubic cell; the multiplicities in the primitive cell are one quarter of those values.

pg	type	position			W	name
O_h	nucleus	0	0	0	4a	Si
O_h	nucleus	1/2	1/2	1/2	4b	Mn
T_d	nucleus	1/4	1/4	1/4	8c	Co
C_{3v}	bond	0.1198	0.1198	0.1198	32f	b_1
C_{3v}	bond	0.6221	0.6221	0.6221	32f	b_2
D_{2h}	ring	0	3/4	3/4	24d	r_1
C_{2v}	ring	0	0.2049	0.2951	48i	r_2
T_d	cage	0	0	0.7357	24e	c

The analysis of the bonding type on hand of the properties of the critical points is discussed in Reference [35]. Metallic systems exhibit a flat electron density ρ throughout the valence region. The flatness $f = \rho_{\min}^c / \rho_{\max}^b$ is a measure of the metallicity. $\rho_{\min}^c$ is the cache critical point, at which the density is minimum, and $\rho_{\max}^b$ is the highest density among all the bond critical points. For Co_2MnSi , it is $f = 0.665$. This is of the same order of magnitude as the flatness in Cu or Fe (both ≈ 0.57 ; see Reference [35]), whereas compounds with covalent bonding typically have f values of less than 0.1. From the large flatness, the bonding in Co_2MnSi is clearly metallic.

Photoabsorption and electron emission spectra have been calculated using single-electron as well as many-electron approaches. The single-particle calculations are based on the full-potential, fully relativistic spin-polarised MUNICH SPR-KKR package of Ebert *et al.* [36]. The results of the electronic structure calculations are the same as those obtained with the FPLAPW scheme of WIEN2k. In particular, the half-metallic character is retained in the fully relativistic calculations, and the semi-relativistic spin-resolved band structures and DOS are nearly identical.

The core-levels themselves are strongly localized in the spherical part of the potential around the nuclei and behave like atomic states. Atomic-type many-particle calculations were performed to explain some details of the Mn $2p$ states in the photon absorption and electron emission spectra. The multiplet calculations were performed using de Groot's program CTM4XAS [37], which includes the effects of the crystal field and charge transfer. The details of the multiplet description and applied methods are given in References [38–40]. For the calculation of the $2p$ excitation, the Slater integrals were scaled to 90% of their value from the Hartree–Fock calculations. The spectra were broadened by 150 to 250 meV according to the experimental resolution. The lifetime broadening was varied over the spectrum, with larger values used for the " $p_{1/2}$ " parts of the spectra to account for Coster-Kronig contributions.

3.2. HAXPES

The polarisation-dependent core-level spectra near the Co and Mn $2p$ excitations are shown in Figures 6 and 8, respectively. It should be emphasised that the spectra were taken from remanently magnetised

samples with no applied external field during the measurement. The magnetic moment is thus only about half of the saturation moment of $5 \mu_B$ (see Section 2). The dichroism in the HAXPES spectra is here quantified by an asymmetry that is defined as

$$A = \frac{I_R - I_L}{\max(I_0 - I_{\text{bg}})}. \quad (1)$$

I_R and I_L are the intensities for opposite helicity; their difference, $I_R - I_L = I_{\text{CD}}$, is the dichroism; $I_0 = I_R + I_L$ is the sum of the intensities; and I_{bg} is the intensity of the background at just above the energy of the $2p_{3/2}$ (or $2p_{1/2}$) excitation, where the dichroism is zero.

Figure 6(a) shows I_0 and I_{CD} in the energy region of the Co $2p$ states. The Co $2p_{3/2}$ excitation appears just above the Mn $2s$ state, which complicates the determination of the background in the energy region away from the Co $2p$ states. A possible dichroism of the Mn $2s$ state is very small and not detectable with the present settings. The Co $2p$ state exhibits a spin orbit splitting of $\Delta_{\text{SO}} = 14.6$ eV into the $2p_{1/2}$ and $2p_{3/2}$ sub-states. I_{CD} exhibits a change of sign in the series $+-+$ across the energy range of the $2p$ excitation. This is typical of a Zeeman-type level ordering in the single-electron model [41]. A pronounced satellite is observed at about 4.3 eV below the $2p_{3/2}$ state but is not detectable at the $2p_{1/2}$ state. The polarisation-dependent spectra and dichroism near the $2p_{3/2}$ state are shown in Figure 6(b). The satellite obviously exhibits negative dichroism. Further, the polarisation-dependent spectra reveal that the main $2p_{3/2}$ excitation exhibits a splitting of about 200 meV. At the same time, the asymmetry, as defined by Equation (1), varies between +17% and -8% across the $2p_{3/2}$ part and between -34% and +25% across the $2p_{1/2}$ part of the spectra. Both the polarisation-dependent spectra and the dichroism indicate that the lines of the multiplet extend over the entire spectral range. In particular, the dichroism does not vanish between the two main parts of the spin-orbit doublet.

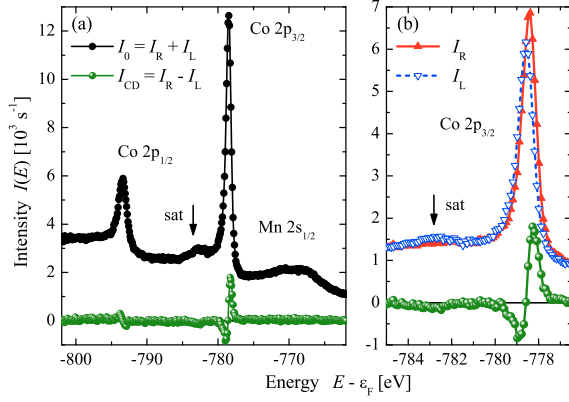


Fig. 6. (Color online) Co $2p$ and Mn $2s$ HAXPES spectra of Co_2MnSi on $\text{MgO}(100)$.

(a) Sum and difference of spectra taken with photons of opposite helicity, (b) spectra at $2p_{3/2}$ taken with σ^+ (R) and σ^- (L) polarisation of the photons. Arrows indicate the "4 eV" satellite.

Figure 7 compares Co $2p$ photoelectron spectra that were calculated using different schemes. In all the calculations, a fixed lifetime broadening was assumed for the complete spectrum to make the single particle and many electron calculations comparable. Therefore, the details of the intensity may differ between the experiment and calculations. Note further that the energy scale of the single electron calculations in Figure 7(a) is related to the ground-state binding energies. Better absolute values for the energies may be found by introducing core holes and using Slater's transition state theory.

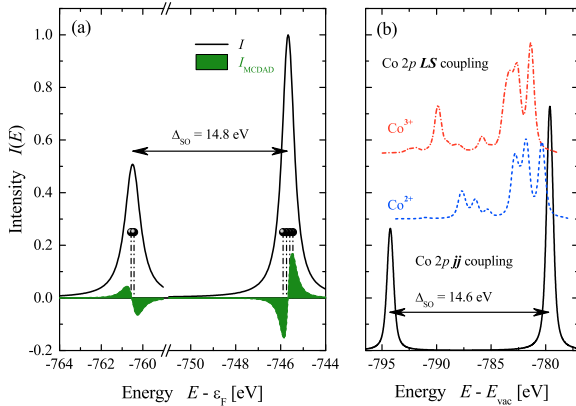


Fig. 7. (Color online) Calculated Co $2p$ photoelectron spectra of Co_2MnSi .

(a) Spectrum and dichroism calculated by SPR-KKR for the solid state (note the x axis break), (b) spectra calculated by CTM4XAS for atoms, assuming different coupling schemes (jj and LS) and states ($2+$ and $3+$) of Co.

Figure 7(a) shows the results of the rela-

tivistic SPR-KKR formalism using the full solid-state potential, whereas Figure 7(b) shows the results of atomic-type Hartree-Fock calculations with CTM4XAS. The atomic-type calculations were performed assuming different states of Co: Co^{2+} and Co^{3+} . The spectra shown in Figure 7(b) are for pure jj and LS couplings. The spectra for LS coupling show typical multiplet structures. Those structures, however, do not appear in the experimental spectra, which show only the spin-orbit doublet and a single satellite. Calculations for intermediate couplings (LSJ) did not improve the situation. This observation is in accordance with multiplet calculations reported by other authors [42].

The splitting of the $2p$ state in jj coupling agrees well with the spin-orbit splitting found in the full relativistic SPR-KKR calculations. The main features of the spectra in the SPR-KKR calculations agree well with the measured spectra, in particular the $+-+$ series of the sign of the dichroism. The 4 eV satellite is not explained by the solid-state calculations. Note that those calculations did not include inelastic or many-body effects. The $2p_{1/2}$ and $2p_{3/2}$ lines are split by the magnetic interactions according to their m_j substates. The positions of the sublevels are plotted with vertical lines in Figure 7(a). The exchange interaction results in Zeeman-type splitting with $\Delta_{exc} \approx 150$ meV between neighbour m_j levels.

The $2p$ spectra of Mn, as shown in Figure 8, exhibit a more complicated structure than the Co $2p$ core level. Splittings of $\Delta_{1/2} = 0.7$ eV and $\Delta_{3/2} = 1.2$ eV are revealed at the $2p_{1/2}$ and $2p_{3/2}$ excitations, respectively. The plot of the total intensity I_0 in Figure 8(b) obviously does not unambiguously reveal a spin-orbit splitting due to the additional splitting of both lines, $2p_{3/2}$ and $2p_{1/2}$. The mean splitting between the doublet-type structure amounts to about $\Delta = 11$ eV. The asymmetry across the $2p_{3/2}$ -type part of the spectrum varies between +48% and -16%. The dichroism does not vanish between the $2p_{1/2}$ and $2p_{3/2}$ lines. This confirms that the splitting is not of Zeemann type, in that case no additional states would appear between the main lines of the spin-orbit doublet.

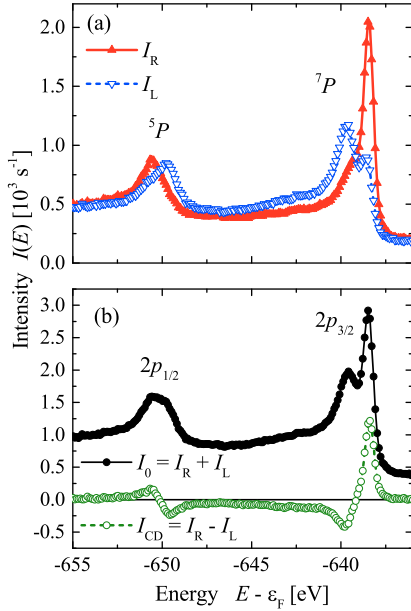


Fig. 8. (Color online) Mn 2p HAXPES spectra of Co₂MnSi on MgO(100).

(a) Spectra taken with σ^+ (R) and σ^- (L) polarisation of the photons, (b) sum and difference of spectra taken with photons of opposite helicity.

The bare intensity spectra (I_0) of the Co and Mn 2p states agree well with spectra taken with linearly polarised photons from bulk material of the isovalent compound Co₂MnGe [43]. The dichroism at the Co 2p states is close to that observed for exchange-biased CoFe or Co₂FeAl films [21]. Here, the asymmetry is lower because of the relaxed resolution used in the present work. Further details of the spectra and dichroism will be discussed after the soft X-ray absorption spectra of the $L_{2,3}$ edges of Mn and Co are presented.

3.3. XAS, XMCD

Figure 9 shows the X-ray absorption spectra and magnetic circular dichroism taken at the $L_{2,3}$ edges of Mn (a) and Co (b). The spectra agree well with those reported by other authors [16, 17, 44–48]. The striking differences in the HAXPES spectra are easily recognised. A splitting of the L_3 edge (corresponding to the $2p_{3/2}$ excitation) is not detectable for either Mn or Co. The spin-orbit splitting of the Co 2p states measured between the L_3 and L_2 maxima amounts to 15.2 eV; thus, it is slightly larger than the value observed in the electron emission spectra. A satellite is observed about 3.5 eV above the L_3 white line of Co. It does not exhibit

any pronounced dichroism and thus should have a different origin from the 4.3 eV satellite observed in electron emission. It might, therefore, not belong to a multiplet-type splitting. Other than in the HAXPES-MCD where the asymmetry changes sign within each line of the doublet, the soft XMCD (SXMCD) of Co does not exhibit a change of sign across the L_3 or L_2 absorption edges. The sign of the SXMCD changes only between the two lines of the spectra. It is opposite at the two different edges and the change of sign takes place at 9.8 eV above the L_3 line.

The asymmetry of the XMCD is defined by

$$A = \frac{I^+ - I^-}{I^+ + I^-}, \quad (2)$$

where $I^\pm$ are the intensities for photon helicity parallel (+) and antiparallel (−) to the magnetic field after background subtraction. At the L_3 edge of Co, it amounts to -33% and has approximately half that value at the L_2 edge.

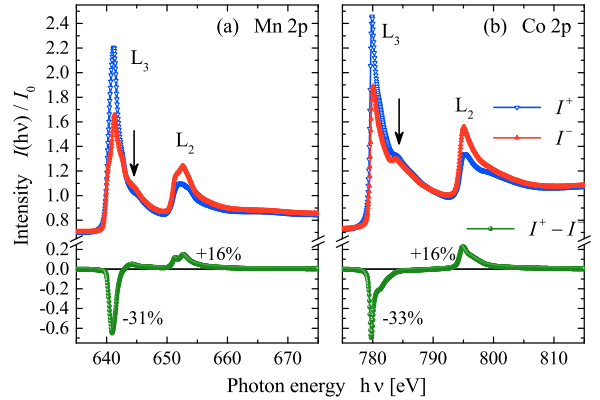


Fig. 9. (Color online) Co and Mn 2p soft X-ray absorption spectra of Co₂MnSi on MgO(100).

(a) Spectra and dichroism taken at the Mn $L_{2,3}$ white line, (b) spectra and dichroism taken at the Co $L_{2,3}$ white line. The intensity is normalised by the photon flux.

The Co $L_{3,2}$ spectrum was calculated with SPR-KKR and is shown in Figure 10. The calculated spectrum contains the 4 eV satellite that appears in the measured spectra. This satellite was previously also observed in other Heusler compounds based on Co₂ [43, 49–52]. It is due to a transition into empty states with high density. It is seen at about 4 eV above the Fermi energy in the majority density of Co, as plotted in Figure 4(b), and also in the unoccupied part of the total majority DOS. Those empty states in photoelectron spectra may also serve as final states for interband transitions from states at

the Fermi energy. Also shown in Figure 10(b,c) are the differential spin and orbital moments that fulfill the differential sum rules [53].

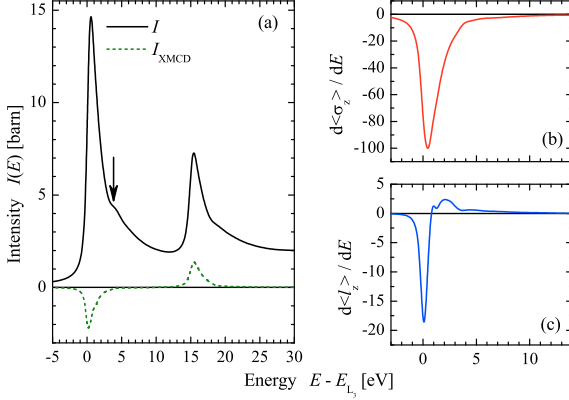


Fig. 10. (Color online) Calculated Co $L_{3,2}$ soft XAS spectrum and XMCD of Co_2MnSi . (a) Spectrum and dichroism, calculated (b) differential spin $\langle\sigma_z\rangle$, and (c) orbital $\langle l_z\rangle$ momentum expectation values. The arrow in (a) marks the 4 eV satellite.

Like the Mn $2p$ electron emission spectra in Figure 8, the absorption spectrum shown in Figure 9(a) exhibits several satellites. The appearance of metallic satellites or multiplet splittings from the exchange interaction is typical of electron emission. The metallic satellites arise from plasmon losses or excitation of interband transitions, as explained for the Co $2p$ spectra. Most striking in the Mn XAS spectra is that the 1.3 eV splitting of the $2p_{3/2}$ state in the HAXPES spectra is not observed at the L_3 absorption edge. The splitting revealed by two maxima in the SXMCD at the L_2 edge is 1.3 eV, which is larger than that observed from the maxima at $2p_{1/2}$ in the electron emission spectrum. It is, however, of the same order as the energy difference of 1.1 eV observed between the negative and positive dichroism maxima in the HAXPES-MCD. The asymmetry at the L_3 edge amounts to -31%. The XMCD changes sign at 1.6 eV above the L_3 maximum. The dichroism does not vanish between the L_3 and L_2 lines, similar to the observation in the electron emission spectra.

In atoms, multiplet splitting is due to the interaction of the nl^{-1} core hole with the polarised open valence shell. The core hole (here $2p^5$) in solids is expected to interact with the polarised d states of the valence band. The localised valence d states, however, are screened by delocalised electrons. The well-known multiplet theory may be used to explain the observed splittings in the spectra [15, 38–40, 54],

assuming that the atomic character of the valence electrons is partially retained in the solid. It was shown above that this approach is critical for Co because of the rather delocalised character of the valence d electrons. Therefore, we will focus on the Mn atoms in Co_2MnSi . The description becomes complicated, as it is not *a priori* clear what ionic state the Mn adopts in the metal. From the electronic structure calculations, one has Mn d^5 , neglecting all the other shells. However, some of the d electrons may be delocalised in the metal and do not contribute to the coupling.

For the multiplet analysis, a Mn $^{2+}$ ionic state with a ${}^6S_{5/2}$ ground state in LSJ coupling is assumed (see [43] for Mn $^{3+}$). Note that the description of the ground states of neutral Mn $^0(4s^23d^5)$ and Mn $^{2+}(4s^03d^5)$ are principally the same because the filled $4s^2$ shell contributes only 1S_0 . According to the dipole selection rules, the following transitions are allowed for the excited states during excitation of the $2p$ core level from $2p^63d^5$ (${}^6S_{5/2}$):

- in electron emission to $\{[2p^53d^5({}^5,7P_J)] + \epsilon(s, d)\}({}^6P_{7/2,5/2,3/2})$,
- or in photon absorption to $[2p^53d^6({}^6P_{7/2,5/2,3/2})]$ and $[2p^53d^5s^1({}^6P_{7/2,5/2,3/2})]$.

The transition schemes given above contain only the leading terms that can be reached according to the selection rules. The final-state p^5d^6 configuration in the absorption scheme contains 1260 terms with a degeneracy of 180, and overall 110 different transitions are allowed by the selection rules, $\Delta J = 0, \pm 1$. In the electron emission scheme, $\epsilon(s, d)$ denotes the ejected electrons with kinetic energy ϵ_k and orbital angular momentum $l' = 0, 2$ for ionisation of the $2p$ shell with $l = 1$. The intermediate ionic states in electron emission obviously have spin values of $S = 5, 7$; thus, the splitting observed in electron emission from the $2p$ core level may be assigned to the spin-exchange splitting of the ionic states. The smaller splitting observed in electron emission from the $2p$ shell corresponds to states with different total angular momentum J of the ${}^7P_{J=4,3,2}$ and ${}^5P_{J=3,2,1}$ intermediate ionic states. The 7P part of the multiplet can be formed only from $2p^5({}^2P)$ and $3d^5({}^6S)$ subshell couplings [55]. In particular, the 7P_4 state has the highest energy in the electron emission spectrum. It is directly related to the $p_{3/2}$ single particle sub-state of a $(jj)J$

coupling scheme

The result of the multiplet calculations for photoexcitation of the $2p$ core level of Mn^{2+} are shown in Figure 11. The line spectra as well as the broadened emission and absorption spectra are shown. The above-mentioned manifold of allowed transitions makes the spectra very complex. Many details of the line spectra are covered, however, by the lifetime broadening.

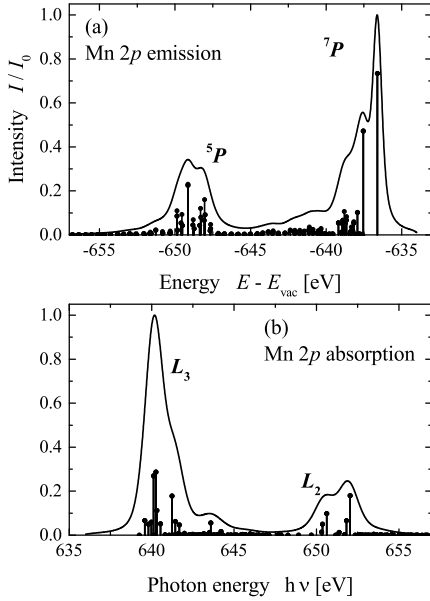


Fig. 11. Calculated Mn $2p$ XPS and XAS spectra. (a) Electron emission spectrum, (b) photoabsorption spectrum.

The calculated electron emission spectrum is shown in Figure 11(a). It was calculated with a crystal field parameter of $10D_q = 1.5$ eV for the initial state of Mn^{2+} . The spectrum exhibits splitting at the 7P ($2p_{3/2}$) and 5P ($2p_{1/2}$) lines. The 7P_4 intermediate ionic state is clearly split off from the remaining spectrum. The multiplet lines related to the 7P part of the spectrum extend over a range of 10 eV. Figure 11(b) shows the photoabsorption spectrum. It was calculated for the ${}^6S_{5/2}$ initial state of Mn^{2+} . The general shape of the spectrum corresponds to that of the measurement. The L_2 white line exhibits a splitting similar to that observed in the experiment. A pronounced feature appears at about 3.5 eV above the maximum of the L_3 white line. Unlike that in the Co spectrum, this satellite is attributed to a multiplet effect.

The further analysis of the XAS and XMCD data is given in the following using the measurements at the Co $L_{3,2}$ edges as an example. The

starting point is the data normalised to the photon intensity. The ‘unpolarised’ total intensity $I_\Sigma = (I^+ + I^-)/2$ is found from the sum of the intensities for the circular polarisation parallel (I^+) and antiparallel (I^-) to the direction of magnetisation. Further, a constant background signal is subtracted such that $I_0 = I_\Sigma - I_{\text{bg}}$. The XMCD signal is given by the difference $I_{\text{MCD}} = (I^+ - I^-)$. The difference does not contain any background; therefore, it can easily be used to reconstruct the polarisation-dependent spectra from $I^\pm = I_0 \pm I_{\text{MCD}}/2$. The total intensity I_0 and the XMCD signal I_{MCD} are plotted in Figures 12 (a) and (b), respectively.

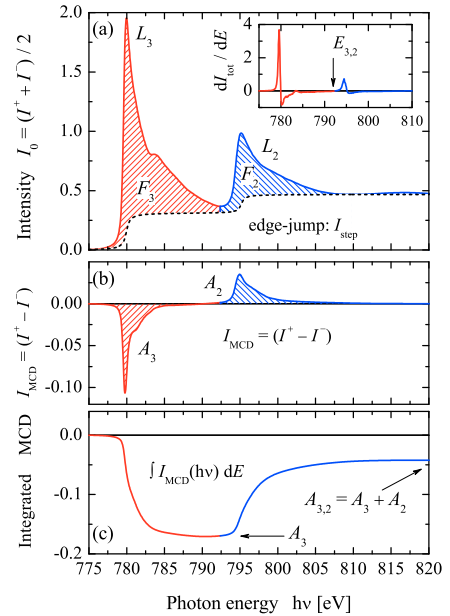


Fig. 12. (Color online) Analysis of Co XAS and XMCD spectra.

(a) XAS spectrum and edge-jump function after a constant background is subtracted [compare Figure 9 (b)], (b) XMCD signal, (c) integrated dichroism. Inset in (a) shows the derivative of the spectrum.

Several energies have to be extracted from the spectra for further analysis, also in view on sum rules. The differentiated total intensity – shown in the inset of Figure 12 (a) – is used for this purpose. The $L_{3,2}$ absorption edges are identified by the maxima of the derivative, and the energies of the maxima of the corresponding white lines are identified by the nearby zero crossings. The energy $E_{3,2}$ for the separation of the L_3 from the L_2 part of the spectrum is taken from the zero crossing of the derivative just in front of the L_2 white line (see arrow in the inset).

The final normalisation of the intensity and

XMCD is performed with respect to the white line intensities after an arctan-type step function, I_{step} , is subtracted for the edge jumps. The step function is modelled by

$$I_{step} = \frac{h}{3} \left[1 + \frac{2}{\pi} \arctan \left(\frac{E - E_3}{w_3} \right) \right] + \frac{h}{6} \left[1 + \frac{2}{\pi} \arctan \left(\frac{E - E_2}{w_2} \right) \right], \quad (3)$$

where h is the height and w_3 and w_2 are the widths of the step function. The latter were set to $w = 350$ meV for both edges. The used prefactors imply a branching ratio of $I_3/I_2 = 2$ for excitation from the p states into delocalised s or d states. The energies E_3 and E_2 for the steps were taken from the maxima of the derivative. In the literature, those energies were sometimes taken from the maxima of the white lines. The width w as well as the step energies E_3 and E_2 influence the quantities that are calculated from the spectra. In this work, tests indicated that variations in the energies and width do not influence the spin magnetic moments by more than 2.5% for Co or 4% for Mn. These variations may be considered small compared to the influence of any variation of the photon polarisation or deviations resulting from the uncertain number of unoccupied d states or other experimental uncertainties.

The area between I_0 and I_{step} is proportional to the number of unoccupied d states and is calculated by integration of $I(E) = I_0(E) - I_{step}(E)$.

$$F = F_3 + F_2 = \int_{E < E_3}^{E_{3,2}} I(E) dE + \int_{E_{3,2}}^{E > E_2} I(E) dE \quad (4)$$

The piecewise integration of F enables calculation of the branching ratio $b_i = F_3/F_2$. Note that the branching ratio is not consistently defined in the literature. In other work, it may be given as the inverse value $r_i = F_2/F_3$ [56] or by F_3/F [57]. Figure 12 (a) shows that $I(E_{3,2}) > 0$ does not vanish at the separation energy $E_{3,2}$, and some intensity of the $2p_{3/2}$ excitation is also found below $2p_{1/2}$. This effect leads to a small underestimation of the branching ratio when b_i is used.

The ratio $q = F_i/h$ of the areas F_i and the height of the step function is a measure of the relative contribution of transitions into localised d states to the absorption spectra [49]. From the data shown in Figure 9, one finds $q_{Co} = 13.2$ eV

and $q_{Mn} = 22$ eV for Co and Mn, respectively. Similarly, from the white line maxima one finds $Q_m = I_{max,L_i}/h$ values of 3.85 and 7.1. Both ratios are larger by a factor of about 2 for Mn than for Co. This hints directly at the stronger localisation of the Mn d valence states.

The areas A_3 and A_2 underneath the XMCD signal [see Figure 12 (b,c)] are needed for the sum rule analysis. They are found by integrating I_{MCD} . Similar to the areas F_i under the intensity, the areas A_i are found by piecewise integration. A_3 is found from integration up to $E_{3,2}$, and the total integral yields $|A_{3,2}| = |A_3| - |A_2|$ because of the opposite sign of the magnetic circular dichroism at the two white lines.

From the sum rule analysis (see References [58, 59]), the spin (m_s) and orbital (m_l) magnetic moments are given by

$$m_s + m_t = \frac{n_d^+}{P_c \cos(\theta)} \frac{A_3 - 2A_2}{F} \mu_B, \\ m_l = \frac{n_d^+}{P_c \cos(\theta)} \frac{2}{3} \frac{A_3 + A_2}{F} \mu_B, \quad (5)$$

where P_c is the degree of circular polarisation, θ is the angle between the magnetisation and the photon momentum, and n_d^+ is the number of unoccupied $3d$ states. The factor n_d^+/F is used to normalise the data. Further, m_t is the magnetic dipole or spin anisotropy term. These equations neglect the effect of different matrix elements. (Please note that the sum rules in Equation (5) are expressed in terms of magnetic moments instead of the expectation values of the spin ($2\langle S_z \rangle$) orbital ($\langle L_z \rangle$) or magnetic dipole ($7\langle T_z \rangle$) operators that are used in some other works (compare Equations (7) and (9) of Reference [60]).)

The partial magnetic moments are found by a sum rule analysis as described above. The bare results (assuming $P_{circ} = 1$ and neglecting jj coupling corrections) are $m_s + m_t = 1.73 \mu_B$, $m_l = 0.02 \mu_B$ for Mn and $m_s + m_t = 0.99 \mu_B$, $m_l = 0.03 \mu_B$ for Co. In the sum rule analysis, $n_{d,Mn}^+ = 4.5$ and $n_{d,Co}^+ = 2.5$ as found from the electronic structure calculations were assumed for the number of d holes in Mn and Co, respectively. For both elements, the magnetic dipole or spin anisotropy term m_t vanishes in the calculations, as expected for cubic crystals. The magnetic moments of Co agree well with the calculations, which predict $m_s = 1.00 \mu_B$ and $m_l = 0.03 \mu_B$.

The sum rule value of the spin magnetic moment of Mn is, however, clearly smaller than the predicted value of $m_s = 3.02 \mu_B$. It is also evident that the total of $\approx (2 \times 1 + 1.73) \mu_B$ found by the sum rule analysis does not match the total magnetic moment of about $5 \mu_B$ found by magnetometry. This behaviour is well known from the literature on the $L_{2,3}$ XMCD from Mn^{2+} . It is usually attributed to jj mixing and overlap of the L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) lines. Goering discusses this in detail in Reference [56]. The spin correction factors were calculated according to that work from the present data and are summarised in Table 3.3. The branching ratio was calculated either from the area ratio $b_i = F_3/F_2$ or the ratio of the intensity maxima $b_m = I_{3/2}^{\max}/I_{1/2}^{\max}$. The *mixing* (X) and *spin correction* (SC) factors are given by [56]:

$$X = \frac{2r-1}{r+1} = \frac{2-b}{1+b},$$

$$SC = \frac{1}{1-2X} = \frac{1}{3} \frac{1+r}{1-r}, \quad (6)$$

where $r = 1/b$ is the inverted branching ratio. The branching ratios are slightly higher than the statistical branching ratio of $b_{\text{stat}} = 2$ as derived from the multiplicity of the p states. Therefore, the spin correction factors are both slightly less than 1. This means, however, that the spin correction factor, in particular that for Mn, does not resolve the discrepancy between the measured and calculated magnetic moments. On the contrary, it will decrease the partial magnetic moments of both Mn and Co.

Table 3. Spin correction factors for Co and Mn $L_{2,3}$ sum rule analysis.

The branching ratio b_m calculated from the intensity maxima is given for comparison. The spin correction factors c_{IE} calculated by Teramura *et al.* [61] are also given.

	integral			b_m	Ref. [61]	
	b_i	X	SC		c_{IE}^{2+}	c_{IE}^{3+}
Co	2.197	-0.062	0.890	2.9	1.096	1.181
Mn	2.135	-0.043	0.921	3.3	1.471	-

An empirical correction factor is usually introduced because of difficulties in correctly determining the magnetic moment of Mn using sum rule analysis. In many publications, the factor $c_{IE} \approx 1.5$ based on the work of Teramura *et al.* is used [61]. Their values are also given in Table 3.3 for Co^{2+} ,

Co^{3+} , and Mn^{2+} . No value could be calculated for Mn^{3+} because L_3 and L_2 could not be separated. Here, the c_{IE} factors of Teramura *et al.* result in a spin magnetic moment of about $2.6 \mu_B$ for Mn and thus a total moment of about $4.6 \mu_B$. Together with the uncertainty about the number of core holes, a spin correction factor of 1.5 is used in the following for Mn, whereas the Co spin magnetic moments are not corrected.

The above reported values concern a single normal incidence measurement. Grazing incidence measurements with $\alpha = 70^\circ$ were performed to study the magnetic anisotropy as proposed by Stöhr and König [62]. The results are summarised in Table 3.3. The normal and grazing incidence measurements differ only slightly; thus, no large anisotropies are expected.

Table 4. Angular dependence of the magnetic moments.

The spin (m_s) and orbital (m_l) moments were measured for normal and grazing photon incidence and are given in multiples of the Bohr magneton μ_B . Mn spin moments are corrected by $c_{IE} = 1.5$.

	Co		Mn	
	m_s	m_l	m_s	m_l
$m_0^{0^\circ}$	0.987	0.0345	2.492	0.0208
$m_0^{70^\circ}$	0.948	0.0341	2.486	0.0202
$m_0^\perp$	0.987	0.0345	2.597	0.0208
$m_0^\parallel$	0.942	0.0341	2.591	0.0202
Δm_0	0.044	0.0004	0.006	0.0006
m_{av}	0.957	0.0342	2.593	0.0204

For uniaxial anisotropy, the angular dependence of the magnetic moments m_0^α and the angle-averaged moment m_{av} [60, 63] are given by

$$m_0^\alpha = m_0^\perp \cos^2 \alpha + m_0^\parallel \sin^2 \alpha,$$

$$m_{av} = (m_0^\perp + 2m_0^\parallel)/3. \quad (7)$$

The average moment may be found from a single measurement at the magic angle, where the second Legendre polynomial becomes zero ($\approx 54.7^\circ$). The effective moment m_{eff} may be rewritten as the sum of the angle-independent spin moment and the angle-dependent dipolar moment m_D [60]:

$$m_{\text{eff}}^\delta = m_s + m_D^\delta, \quad (8)$$

where $\delta = \perp$ or $\parallel$ represent the perpendicular or parallel components with respect to the film plane, respectively. The orbital moments are already very small; therefore, an analysis of their anisotropy is not reliable. The dipolar moments of the Mn atoms are also negligible, as seen from the very small difference Δm_0 (see Table 3.3). For the Co atoms, the difference Δm_0 is about 5%, and the resulting perpendicular and parallel components of the dipolar moment are $0.03 \mu_B$ and $-0.015 \mu_B$, respectively. From those values, the out-of-plane component is larger than the in-plane component. A nearly vanishing anisotropy is also expected because of the small coercive field (H_c). From the Stoner–Wolff model, the anisotropy energy is on the order of

$$K = \frac{1}{2} H_A \times \mu_0 M_{\text{sat}}. \quad (9)$$

The present films have $\mu_0 H_c = 4$ mT ($H_c = 0.3$ kA/m), and their magnetic moment of $m_s = 5 \mu_B$ corresponds to a saturation magnetisation of $M_{\text{sat}} = 260$ kA/m. Those values result in an expected anisotropy energy that is smaller than 0.5 kJ/m³, assuming that the coercive field is on the order of the anisotropy field ($H_A \approx H_c$). This agrees also with the fact that the dipolar term m_D nearly vanishes in accordance with the vanishing of m_t in the ab-initio calculations of the electronic structure.

The XMCD spectra were further used to determine the unoccupied electronic structure as described in References [18,64]. The spin-resolved unoccupied density of d states is calculated as

$$n_{d_j}^{\uparrow,\downarrow}(E) = I_0(E) \pm \frac{1}{P_j} I_{\Delta}(E). \quad (10)$$

$I_0 = (I^+ + I^-)/2$ is the isotropic absorption coefficient (after step-function-type background subtraction), and $I_{\Delta} = (I^+ - I^-)/2$ is half of the magnetic dichroism signal. P_j is the spin polarisation obtained for excitation from the $p_{3/2}$ ($P_{3/2} = 1/4$) and $p_{1/2}$ ($P_{1/2} = -1/2$) states (see Reference [65], page 391). The upper and lower sign correspond to the majority ($n^{\uparrow}$) and minority ($n^{\downarrow}$) densities, respectively. Note that this is an approximation to the DOS because the measured absorption spectra also contain cross section, lifetime, and many-particle effects, which are all energy dependent.

Figure 13 compares the unoccupied partial d DOS of Co and Mn in Co_2MnSi . The unoccupied PDOS is derived from the $L_{3,2}$ edges of the XMCD

data using the spin-resolved unoccupied PDOS function (see Equation (10) and References [18,64]). The calculated, raw DOS as shown in Figure 4 was convoluted by the Fermi-Dirac distribution at 300 K and a Gaussian with a width of 300 meV, to account for experimental and lifetime broadening. The majority and in particular the minority PDOS of Co and Mn are well resolved and in particular the minority PDOS's agree quantitatively with the calculated ones. The measured Co PDOS exhibits a shift of the majority states with respect to the high density of minority states just above ϵ_F . The shift is a consequence of the itinerant $3d - t_{2g}$ bands that dominate the unoccupied majority states at the Fermi energy (see Figure 4). The interaction of the core hole in the final state with localized $3d$ states lowers the transition energy. The decrease of the transition energy is less for itinerant state because they screen the core hole to some extent [66,67]. The different core-hole screening thus produces an energy shift between itinerant and localized states. A correlation energy of $\Delta E_c = 0.5$ eV was suggested in Reference [18]. An increase in the unoccupied majority states at Co is clearly visible at about 4 eV for both the calculated and measured PDOS. This high density is responsible for the 4 eV satellite observed in the Co $2p$ photo absorption and electron emission spectra. The minority PDOS of Mn shows a pronounced maximum at about 1 eV. In contrast, a characteristic double step increase is observed at the measured majority PDOS of Mn. An energy shift of $\delta E \approx 1.1$ eV is determined from the derivative of the PDOS (see Inset in Figure 13). This is in the same order as the shift observed for bulk Co_2MnSi material and is characteristic of Heusler alloys [64,68,69]. It is induced by electron correlation effects between core hole and localised or itinerant minority states. Indeed, the correlation energy ΔE_c may strongly change the minority PDOS determined from the XMCD measurements. As a consequence, the half-metallic ferromagnetism is not unambiguously detectable with the used method.

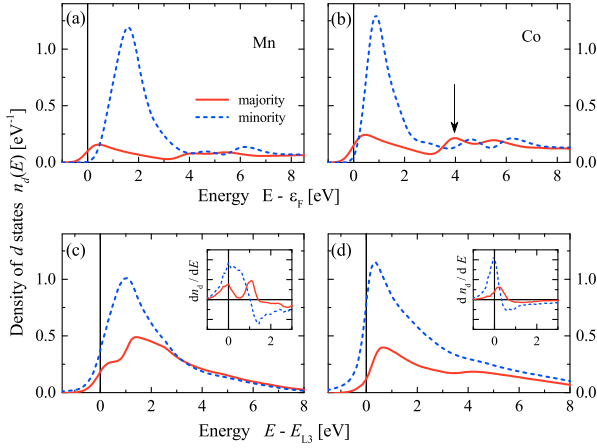


Fig. 13. (Color online) Unoccupied, spin-resolved partial d DOS of Co and Mn.

Shown are the partial densities of d states (PDOS) from first principles calculations (a, b) and the PDOS taken from the Mn $L_{2,3}$ and Co $L_{2,3}$ absorption data (c, d). Insets in (c) and (d) show the derivatives of the experimental data. The calculated PDOS is convoluted by the Fermi-Dirac distribution at 300 K and a Gaussian with a width of 300 meV. (Note the different zeros (ϵ_F or E_{L_3}) of the energy scales.)

4. Summary and Conclusions

The $2p$ core levels of Co and Mn in the HMF Co_2MnSi were investigated by hard X-ray photoelectron and soft X-ray photoabsorption spectroscopies. Magnetic dichroism in HAXPES and XAS were used to explain the states of Co and Mn in thin films made of this intermetallic compound. A combination of *ab-initio* calculations and core-level spectroscopy with circularly polarised photons showed that the Mn d valence electrons and the accompanying magnetic moments have a localised character, whereas the Co d valence electrons result in an itinerant magnetic moment.

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