

Insights into the electronic structure of Co_2FeSi from x-ray magnetic linear dichroism

Markus Meinert,^{1,*} Jan-Michael Schmalhorst,¹ Manuel Glas,¹ Günter Reiss,¹ Elke Arenholz,²
Tim Böhner,³ and Kornelius Nielsch³

¹*Thin Films and Physics of Nanostructures, Department of Physics, Bielefeld University, D-33501 Bielefeld, Germany*

²*Advanced Light Source, Lawrence Berkeley National Laboratory, California 94720, USA*

³*Institute of Applied Physics, University of Hamburg, Jungiusstrasse 11, D-20355 Hamburg, Germany*

(Received 31 January 2012; revised manuscript received 22 May 2012; published 14 August 2012)

Experimental evidence both for and against a half-metallic ground state of the Heusler compound Co_2FeSi has been published. Density-functional-theory-based calculations suggest a non-half-metallic ground state. It has been argued that on-site Coulomb interaction of the d electrons has to be taken into account via the LDA+ U method, which predicts a half-metallic ground state for $U \approx 2.5, \dots, 4.5$ eV. X-ray magnetic linear dichroism (XMLD) can be used as a tool to assess the appropriateness of the LDA+ U approach: The calculated spectra within the LDA+ U or GGA+ U schemes are different from those within the LDA or GGA. Due to its ability to separate different orbital symmetries, XMLD allows us to distinguish between different models of the electronic structure of Co_2FeSi . In this article we discuss experimental XMLD spectra and compare them with detailed first-principles calculations. Our findings give evidence for the inadequacy of the LDA+ U or GGA+ U band structures, whereas constrained calculations with the GGA and a fixed spin moment of $6 \mu_B$ give better overall agreement between experiment and theory.

DOI: [10.1103/PhysRevB.86.054420](https://doi.org/10.1103/PhysRevB.86.054420)

PACS number(s): 71.20.Lp, 75.70.-i, 78.70.Dm, 75.50.-y

I. INTRODUCTION

Half-metallic Heusler compounds of the type Co_2YZ (with Y a $3d$ transition metal and Z an sp main group element) are promising materials for spin electronics. They were shown to follow the Slater-Pauling rule, which gives their magnetization per formula unit as $m = N_v - 24$, where N_v is the number of valence electrons.¹ Co_2FeSi is the Heusler compound with the highest observed magnetization of nearly $6 \mu_B$ per formula unit.²

The electronic structures of half-metallic Heusler compounds are routinely computed within the framework of density functional theory (DFT). The local (spin) density and generalized gradient approximations (LDA or GGA) are often able to reproduce the observed ground-state magnetic moments in agreement with experimental data. However, Co_2FeSi is a case, for which these approximations fail: The calculated magnetic moment is too low and the density of states is not half-metallic. Because of this, approaches to go beyond the (semi-)local approximations were tested. Applying LDA+ U in the fully localized limit with U around 4 eV opens a minority gap around E_F and consequently gives the full magnetic moment.² Calculations with the nonempirical hybrid PBE0 functional resulted in a half-metallic ground state with a 1-eV wide minority gap.³ The LDA+ U (or GGA+ U) approach has been applied to study the electronic structure of Co_2FeSi and related compounds.⁴⁻⁸

Although Co_2FeSi satisfies the Slater-Pauling rule and has a near-integer magnetic moment per formula unit, which is a necessary condition for half-metallic ferromagnetism, there is some experimental evidence to the contrary. Tunnel magnetoresistance experiments show rather low TMR with Co_2FeSi electrodes, and the conductance curves lack characteristic features of the minority gap.^{9,10} Furthermore, the Gilbert damping is quite high.¹⁰ On the other hand, a temperature-independent resistivity is observed for bulk single- and polycrystalline Co_2FeSi below 50 K, which is seen as a fingerprint of half-metallicity.¹¹

Recently, Kallmayer *et al.* predicted from first-principles calculations the x-ray magnetic linear dichroism (XMLD) of Co_2FeSi within the LDA and the LDA+ U schemes.¹² No significant differences of the x-ray absorption or circular dichroism spectra were predicted. However, clearly different XMLD spectra were computed, and XMLD was proposed as a tool to determine which electronic structure is actually present in Co_2FeSi . In this article we use the proposed method on epitaxial thin films of Co_2FeSi .

The article is organized as follows: Secs. II and III describe the experimental conditions and details of our computational approach. The results of the x-ray magnetic circular (XMCD) and linear dichroism measurements and calculations are presented in Sec. IV, followed by a discussion of the results in Sec. V. The main part of this article is focused on the understanding of the XMLD of Co_2FeSi . To make sure that the dichroic signals are intrinsic to Co_2FeSi , we investigated samples prepared with different deposition conditions.

II. EXPERIMENT

Epitaxial thin films of Co_2FeSi have been grown on MgO(001) substrates by dc and rf magnetron co-sputtering with and without seed layers and various heat treatments.

The samples were deposited with a co-sputtering tool with 3-inch sputter sources. It allows heating of the substrates to 900 °C. The base pressure was typically 2×10^{-9} mbar, and the Ar working pressure was 2×10^{-3} mbar. The target-to-substrate distance was 21 cm. Elemental Co, Fe, and Si targets of 99.9% purity were used. The metals were dc sputtered and Si was rf sputtered. The MgO capping layers were deposited by electron beam evaporation.

We distinguish two types of samples, which are explained in Table I: CFS-Cr (with Cr seed layer and postannealing) and CFS-HTD (high-temperature deposition without seed layer).

X-ray absorption (XAS), x-ray magnetic circular (XMCD), and linear dichroism (XMLD) spectra were taken at beamline

TABLE I. Preparation conditions of the samples.

Name	Stack (thicknesses in nm)
CFS-Cr	MgO(001)/Cr 5/700°C <i>in situ</i> /CFS 20 @ RT/Mg 0.5/MgO 1.0/450°C <i>ex situ</i>
CFS-HTD	MgO(001)/CFS 20 @ 700°C/Mg 0.5/MgO 1.0

4.0.2 of the Advanced Light Source, Berkeley. Magnetic fields of 0.55 T were applied to magnetically saturate the samples. XMCD spectra were taken with an angle of 30° between the beam and the sample surface; the magnetic field was parallel to the beam. The circular polarization degree was 90%. XMLD spectra were taken in normal incidence, with the magnetic field canted out of the sample plane by 10°. The degree of linear polarization was 100%. The magnetization was switched at every photon energy to obtain the dichroic spectra. All measurements were taken at room temperature, which is justified in view of the high Curie temperature of Co₂FeSi. Surface sensitive total electron yield spectra (TEY) were taken concurrently with transmission spectra. The transmission signal was collected by a photodiode behind the sample, which measured the x-ray luminescence in the substrate.¹³ The beamline resolution was about 0.1 eV.

Structural characterization was performed by x-ray diffraction in a Philips X'Pert Pro MPD diffractometer with a Cu anode. Bragg-Brentano optics were used for the specular measurements, and an open Eulerian cradle in combination with collimator point-focus optics was applied for off-specular measurements.

Film compositions were determined by x-ray fluorescence spectroscopy, which has been cross-checked with inductively coupled plasma optical emission spectroscopy. The film stoichiometries were thus adjusted to Co_{50±2}Fe_{25±1}Si_{25±1}.

Magnetization measurements have been performed with a vibrating sample magnetometer at 50 and 300 K in magnetic fields up to 3 T.

III. COMPUTATIONAL APPROACH

The computational work was carried out within the ELK code,¹⁴ which is based on the full potential linearized augmented plane waves (FLAPW) method. Various approximations to the exchange-correlation functional were tested. Within the generalized gradient approximation (GGA), we chose the Perdew-Burke-Ernzerhof (PBE) functional.¹⁵ We performed LDA+*U* calculations, based on the Perdew-Wang local (spin) density approximation (LDA).¹⁶ The fully localized limit (FLL) was adopted, as formulated by Liechtenstein *et al.*¹⁷ In addition, we performed GGA+*U* calculations as well. In both cases, we neglect multipole components in the expansion of the Coulomb interaction by using only the *U* parameter, and setting the intra-atomic exchange parameter $J = 0$. Thus, $U_{\text{eff}} = U - J = U$, and the Slater integrals F^2 and F^4 are zero. In LDA+*U*/GGA+*U* calculations, one often chooses the *U* parameter such that the experimental magnetic moment or band gap is reproduced.

As another route to obtain an electronic structure with the full magnetic moment, we use the PBE functional and enforce the experimental (or Slater-Pauling) magnetization within a

fixed spin moment (FSM) calculation. Thus, we obtain the (variationally unique) PBE band structure with the lowest energy, that results in the desired magnetization.¹⁸ This method is usually used to map the dependence of the total energy on the magnetization. Here, we use it to model the unoccupied states of Co₂FeSi, such that the minority *d*-states above the gap are shifted above the Fermi energy (see the upper part of Fig. 6 for a comparison of GGA and GGA FSM results). We have performed the calculations with a fixed total spin moment of $6 \mu_B/\text{f.u.}$

The muffin-tin radii R_{MT} were set to 2.2 a.u. for all atoms, and the plane-waves cutoff was set to $R_{\text{MT}} \times k_{\text{max}} = 8.0$. The angular momentum expansion in the muffin tins was taken to $l_{\text{max}} = 10$ for both the wave functions and the potential. The maximum **G**-vector length for the density and potential expansion in the interstitial was set to $|\mathbf{G}|_{\text{max}} = 14.0 \text{ a.u.}^{-1}$. **k**-point meshes of $20 \times 20 \times 20$ points, restricted to the irreducible wedge of the Brillouin zone, were used. Spin-orbit coupling was included by the second-variational method. The $2p$ core states were described as (scalar relativistic) local orbitals (i.e., the $2p_{3/2}$ and $2p_{1/2}$ state have the same basis function). This can give rise to a small error for the $2p_{1/2}$ state, when compared to a fully relativistic description of the core states. Exchange splitting of these states is taken into account. X-ray absorption spectra were computed within the Kubo linear response formalism as lined out in Ref. 19. All theoretical spectra are broadened with a 0.3-eV wide (FWHM) Lorentzian to account for lifetime broadening.

Experimental lattice parameters of CFS were reported to be 5.64 and 5.66 Å.^{2,11} We used the average value (5.65 Å) for our calculations.

IV. RESULTS

A. Structural characterization

The samples were epitaxial with a [001] orientation. The out-of-plane lattice parameters are close to the bulk values (Table II). The structural ordering is given by the long-range order parameters S_{B2} and S_{L2_1} .²⁰

$L2_1$ order is observed for both samples, and the order parameters S_{B2} are close to 1 for CFS-Cr and CFS-HTD (Table II). The x-ray scattering amplitudes of Co and Fe are very similar, thus we cannot detect chemical disorder between

TABLE II. Structural properties of the samples: out-of-plane lattice constants, B2 and $L2_1$ order parameters, and rocking curve full width at half maximum. Unit of $\Delta\omega$ is degrees.

Name	a (Å)	S_{B2}	S_{L2_1}	$\Delta\omega$
CFS-Cr	5.62	0.97 ± 0.02	0.8 ± 0.05	1.6
CFS-HTD	5.65	0.98 ± 0.02	1.0 ± 0.05	0.5

Co and Fe. Therefore, S_{B2} measures the disorder between Si and Co sites, which is virtually zero. S_{L2_1} measures the disorder between Si and Fe sites; we observe a high degree of $L2_1$ order for both samples. While CFS-HTD has approximately full $L2_1$ order, we find a slightly reduced ordering for CFS-Cr, with about 10% of the Fe sites occupied by Si. Note the larger experimental uncertainty for S_{L2_1} due to defocusing of the x-ray beam in off-specular measurements.

CFS-HTD has an x-ray reflectometry profile that indicates island growth. The real structure of this film is similar to what was observed by Schneider *et al.*²¹ (i.e., a discontinuous film). CFS-Cr has a smooth surface. The rocking curve widths $\Delta\omega$ (reflecting the crystalline orientation distribution) are very different for the two samples, being small for CFS-HTD and rather large for CFS-Cr.

B. X-ray magnetic circular dichroism

In Fig. 1 we exemplarily show the x-ray magnetic circular dichroism spectra obtained in total electron yield on sample CFS-Cr.

All characteristic features that have been observed by other authors for Co_2FeSi are present in our XAS/XMCD spectra as well: the shoulders on the trailing edges of the absorption edges, and the feature in the Co spectra 4 eV above the absorption onset.^{2,12} The latter arises from an s - d hybrid state of Co and Si. The luminescence spectra (not shown) are in good agreement with the TEY data.

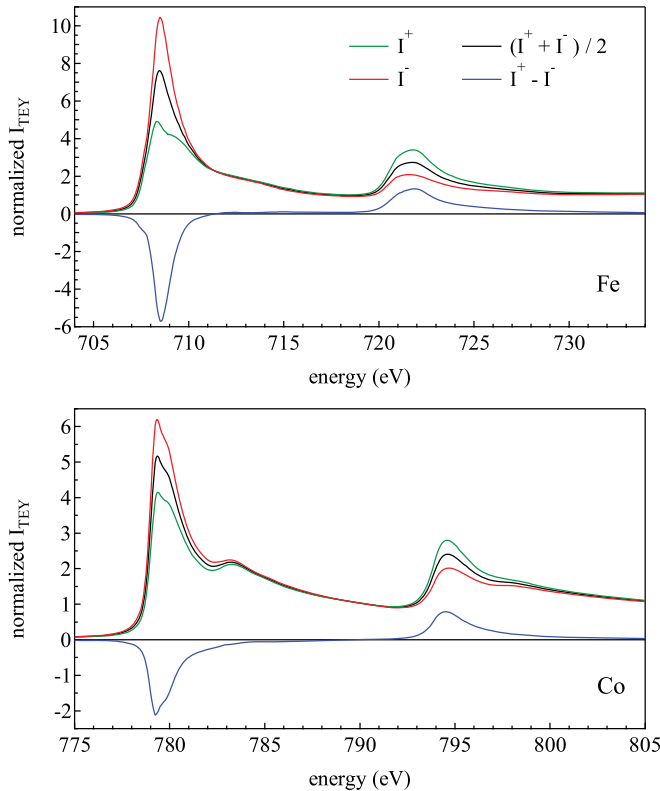


FIG. 1. (Color online) X-ray absorption and magnetic circular dichroism spectra of the sample CFS-Cr taken in total electron yield. The absorption spectra are normalized to unity 40 eV above the L_3 absorption onset.

TABLE III. Element-resolved magnetic spin and orbital moments of CFS-Cr obtained from sum rule analysis of the TEY and luminescence spectra. All moments are given in μ_B .

	m_s^{TEY}	m_s^{Lum}	m_l	m_l/m_s
Co	1.32 ± 0.2	1.38 ± 0.2	0.10 ± 0.01	0.077
Fe	3.17 ± 0.4	3.01 ± 0.4	0.09 ± 0.01	0.030

The element specific magnetic moments are extracted from a sum rule analysis of the spectra, assuming the radial $p \rightarrow d$ transition matrix constants $C^{\text{Fe}} = 6.6$ eV and $C^{\text{Co}} = 7.8$ eV according to Ref. 23. The spin moment ratio determined from TEY is $m_s^{\text{Fe}}/m_s^{\text{Co}} = 2.4 \pm 0.3$, whereas the ratio from luminescence detection is $m_s^{\text{Fe}}/m_s^{\text{Co}} = 2.2 \pm 0.3$. Both samples have extrapolated low-temperature magnetizations of $6.1 \pm 0.2 \mu_B/\text{f.u.}$ (determined by VSM); using this value to scale the XMCD sum rule results, we find element-resolved moments as given in Table III. The scaling removes experimental uncertainties with respect to the magnetic saturation of the samples.

With the white line sum rule from Ref. 22, we obtain the numbers of d holes: $N_h^{\text{Co}} = 3.0 \pm 0.4$ and $N_h^{\text{Fe}} = 4.3 \pm 0.6$, which are significantly higher than the values for the pure elements (2.4 and 3.45, respectively).²³ The analysis of the sum rules rests on the assumption that the radial $p \rightarrow d$ transition matrix constants are independent of the chemical environment. This might be true within about 10% and gives rise to a corresponding error. Furthermore, there is some uncertainty due to the background subtraction, which we estimate to be of the order of 10% as well.

C. X-ray magnetic linear dichroism

The XMLD is generally measured as the difference between two absorption spectra taken with linearly polarized light; one with the polarization vector parallel to the magnetization, and one perpendicular. It is expressed with TEY intensities as $\text{XMLD} = I_{\text{TEY}}^{\parallel} - I_{\text{TEY}}^{\perp}$. The XMLD has a large crystal anisotropy. It was shown for cubic systems that all XMLD spectra can be described as a linear combination of two fundamental spectra, which are measured along the [100] and [110] high symmetry directions, respectively.²⁴ Earlier reports of XMLD of Heusler compounds include Co_2MnSi and Co_2MnAl ,²⁵ Mn_2CoGa and Mn_2VGa ,²⁶ and Co_2TiSn .²⁷

The XMLD spectra of CFS-Cr are presented in Figs. 2 and 3. The spectra have pronounced substructures, and the intensities are quite large. For Co, the maximum XMLD intensity is found in the [110] direction at the L_3 edge, and amounts to 7.1% with respect to the L_3 resonance height. The maximum intensity for Fe is observed at the L_3 edge in the [100] direction, and it amounts to 6.9%. For Co, the maximum XMLD is twice as large in the [110] direction than in the [100] direction. In contrast, for Fe the signal strengths are similar in the two fundamental directions.

Comparing the Co XMLD spectra with the available published data of other Heusler compounds, we note that the [110] spectra are very similar in all cases (Co_2MnSi , Co_2MnAl , Co_2TiSn , and Mn_2CoGa).^{25–27} The only exception is Co_2MnSi , which has a sharper, and more detailed structure.

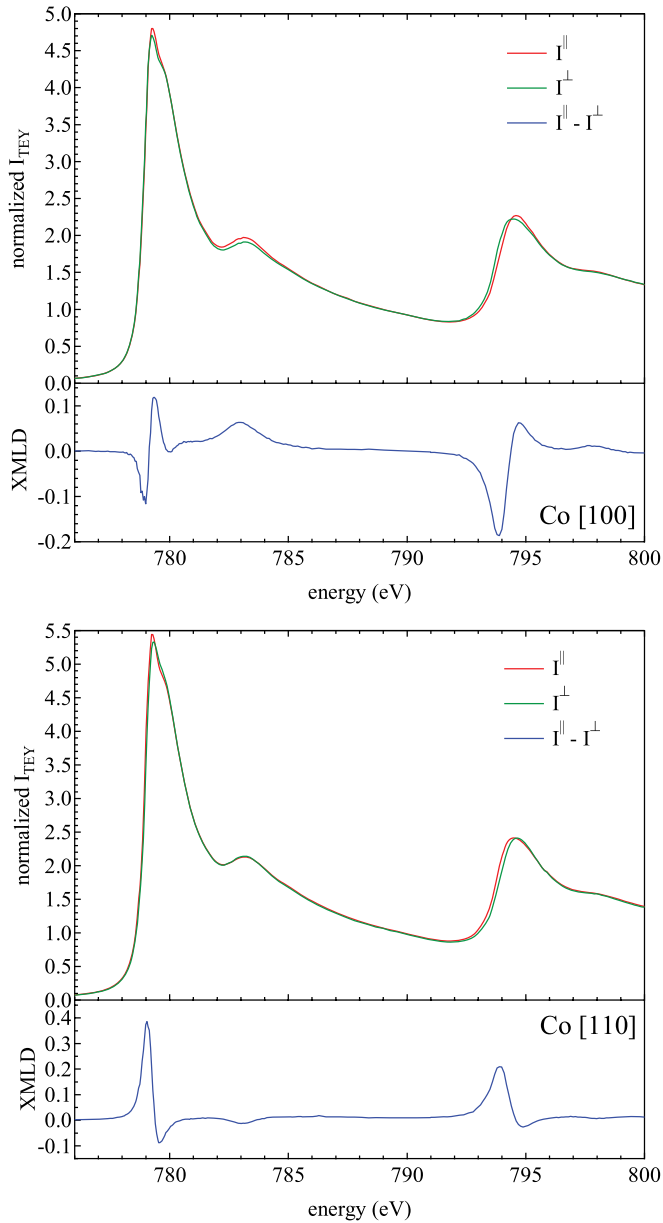


FIG. 2. (Color online) Fundamental x-ray magnetic linear dichroism spectra of Co in Co_2FeSi , taken in total electron yield. The normalization is the same as in Fig. 1.

Telling *et al.* ascribe this (in particular in comparison with Co_2MnAl) to the half-metallic character of Co_2MnSi and the associated localized character of the d electrons.²⁵ This could hint at the lack of half-metallic character in Co_2FeSi .

It has been demonstrated that the XMLD of Heusler compounds depends on the square of the spin moment, modified by the degree of localization of the magnetic moment.^{25–28} The maximum Co XMLD intensity along [110] at the L_3 edge as a function of the square of the Co spin moment ($4.1\%/\mu_B^2$, using the TEY values for consistency) is weaker than for Co_2MnAl ($4.79\%/\mu_B^2$), Co_2MnSi ($7.6\%/\mu_B^2$), or Co_2TiSn ($5.93\%/\mu_B^2$). The heights of the L_3 resonances with respect to the background are comparable among these compounds, so this normalization is reasonable. This hints at not fully localized Co moments, and indicates the lack of

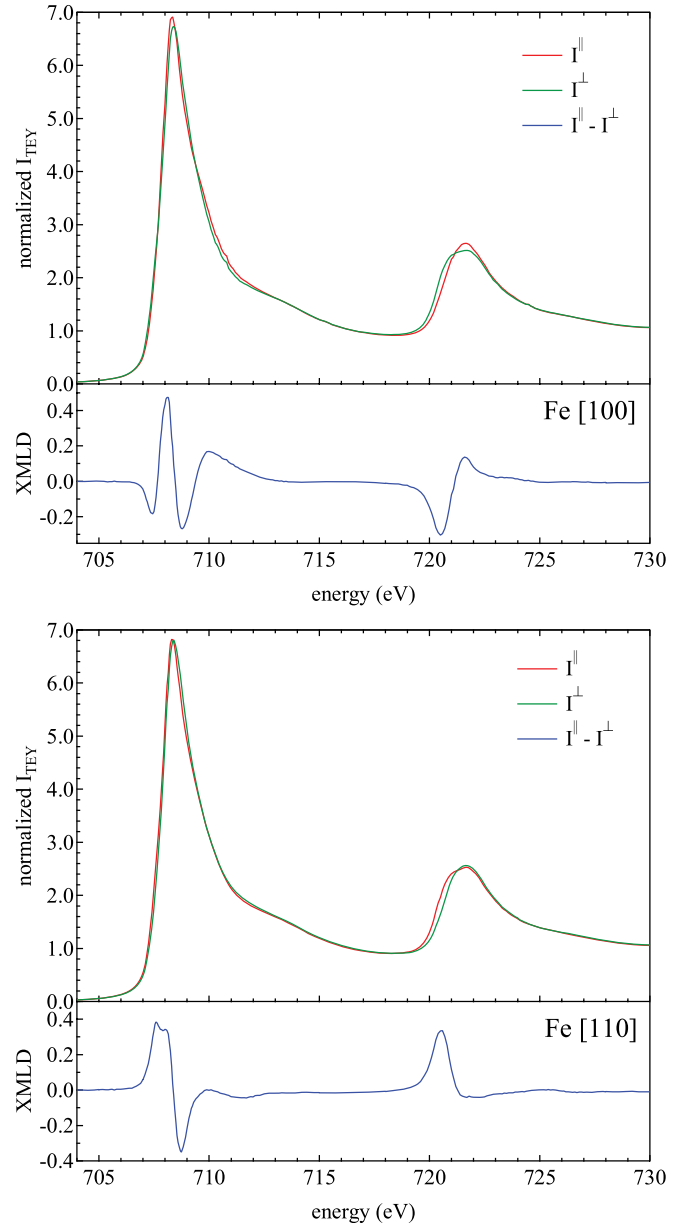


FIG. 3. (Color online) Fundamental x-ray magnetic linear dichroism spectra of Fe in Co_2FeSi , taken in total electron yield. The normalization is the same as in Fig. 1.

half-metallicity as well. Still, Co_2FeSi has the largest XMLD observed for Co in a Heusler compound due to its large magnetic moment.

The Co [100] XMLD spectrum of Co_2FeSi is different from the spectra of the other compounds mainly by a positive contribution at the maximum of the L_3 resonance, which is very weak in the other cases.

XMLD spectra of Fe containing Heusler compounds are not available in the literature. However, our spectra are clearly different from XMLD spectra of pure Fe films grown on GaAs(001).²⁹ Notably, the Fe spectra of Co_2FeSi are similar to the Mn XMLD spectra of Co_2MnSi .²⁵ The [110] spectra have a double-peak contribution at the low-energy side of the L_3 edge and a negative contribution at the high-energy side. The L_2 edge is even more similar. For the [100] direction we observe

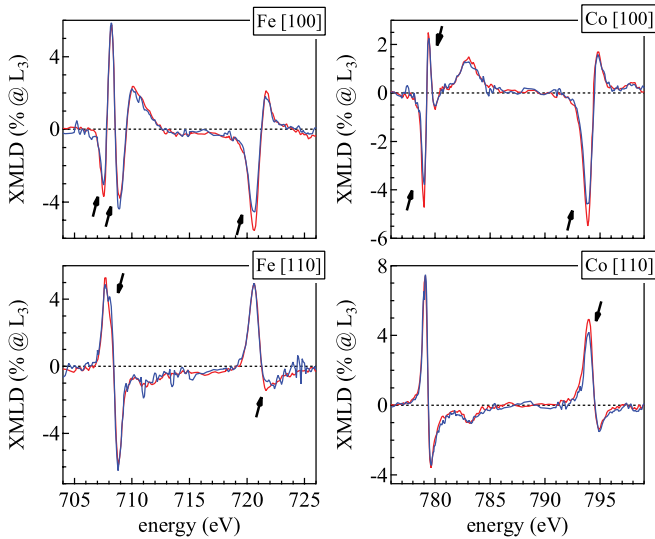


FIG. 4. (Color online) X-ray magnetic linear dichroism spectra of the samples CFS-HTD (red traces) and CFS-Cr (blue traces). The spectra were taken in luminescence detection. Subtle differences in the intensities of the various features are visible (see arrows).

a similar resemblance, but Mn has a small positive contribution at the absorption onset, which is missing for Fe. The maximum XMLD intensity of Fe as defined above ($0.69\%/ \mu_B^2$) is close to that of Mn in Co_2MnSi ($0.77\%/ \mu_B^2$) or Co_2MnAl ($0.68\%/ \mu_B^2$),²⁵ and larger than in pure Fe ($0.54\%/ \mu_B^2$).^{28,29} Fe and Mn occupy the same site of the Heusler structure and experience similar local crystal fields. The larger XMLD intensity of Fe in Co_2FeSi compared to pure Fe indicates a more localized character of the magnetic moment. These findings emphasize the high site specificity of the XMLD and its sensitivity to the local crystal field.

In Fig. 4 we compare the XMLD spectra of our samples taken in luminescence detection mode. The intensities are given as percentages of the L_3 absorption peak. The main purpose of this comparison is to verify that the XMLD spectra are essentially independent of the deposition conditions and specific details of the films. The various spectra are very similar throughout the samples, and only small differences are seen for the intensities of individual features. These differences may be associated with the slightly lower degree of $L2_1$ ordering in the CFS-Cr sample.

D. First-principles calculations

Four computational approaches are compared with experiment: plain GGA, GGA fixed spin moment (FSM), LDA+ U ($U = 4.5$ eV), and GGA+ U ($U = 1.9$ eV). For LDA+ U we adopt the U value of Refs. 2,12. In our GGA+ U approach, we can use a slightly lower U than in LDA+ U to obtain the full magnetic moment. In the latter case, at least 2.5 eV are required; here, we adopt the smallest value that results in the full magnetic moment. This value was also used in Ref. 4 within a GGA+ U approach. The total magnetic moment neglecting spin-orbit coupling with the plain GGA (with the PBE functional) is $5.53 \mu_B$, which is in good agreement with previously reported values.⁵ Figure 5 shows the theoretical and

experimental spectra for Co and Fe along the [100] and [110] directions.

The general shape of the GGA spectra is quite similar to the experimental ones, but the width of the theoretical curves is considerably too small. The GGA FSM description improves considerably the width and general shape of the spectra, and gives a very good overall resemblance of the experimental data of Co [100] and [110], and Fe [100].

In contrast, both the LDA+ U and GGA+ U spectra do not describe the experimental data. For Fe [100], the L_3 spectra are inverted, and the Co spectra have spurious substructures. Further, the Co spectra are broader than the experimental data. The computed d band width is consequently too large.

The Fe [110] spectra are very similar in the GGA, GGA FSM, and LDA/GGA+ U approaches. All of them have a negative contribution at the absorption onset, which is positive in the experiment. Some features at the high energy side of the L_3 edges in the experimental spectra are not captured by any theoretical approach—these are marked with arrows in Fig. 5. In the Co spectra, these features are associated with the Co-Si s - d hybrid state. Since our one-electron theory fails to describe these features, we conclude they are associated with many-body effects.

Electron-hole correlations, in particular the formation of bound excitons (which lead to the so-called “multiplet” splittings in the absorption spectra), are often observed in the $L_{3,2}$ x-ray absorption spectra of $3d$ transition metal atoms in insulators. However, these effects are virtually absent in the spectra of metals, and reduce to a change in the branching ratio away from the statistical 2:1 in the early $3d$ transition metals. Laskowski and Blaha have shown by solving the Bethe-Salpeter equation in an all-electron framework that the dielectric response of the system plays a crucial role for these effects.³⁰ The formation of the splittings is governed by the screened Coulomb interaction of the excited electron with the core hole. In a (half-)metal, this interaction is exponentially screened out, so that only small changes of the spectra remain. In a recent paper we have demonstrated that this effect is of the order 0.3 eV for Co in Co_2TiSn by means of core-hole calculations in the independent-particle approximation,²⁶ whereas the unoccupied d band width is of the order 2 eV here. Thus, due to the metallic screening of the Coulomb interaction it is reasonable to assume that independent-electron calculations can give a good description of the x-ray absorption spectra of Co_2FeSi .

From the comparison of the calculations, it becomes clear that GGA FSM provides the best overall matching of the experimental data, and can serve to model the unoccupied band structure of Co_2FeSi . Based on the GGA FSM electronic structure we have computed the number of d holes of Fe and Co. This has to be done with care in the FLAPW method, because these numbers depend on the choice of the muffin-tin radii. Therefore we computed the hole numbers with different choices of muffin-tin radii and selected the ones for which the partial magnetic moments saturate—the relevant part of the d orbitals is then presumably entirely contained in the muffin tins. These radii (2.2 a.u.) were used for all calculations throughout this work (muffin-tin radii of 2.28 a.u. correspond to maximum space filling). The corresponding numbers of d holes are $N_h^{\text{Co}} = 2.9$ and $N_h^{\text{Fe}} = 4.1$. Both are a bit smaller

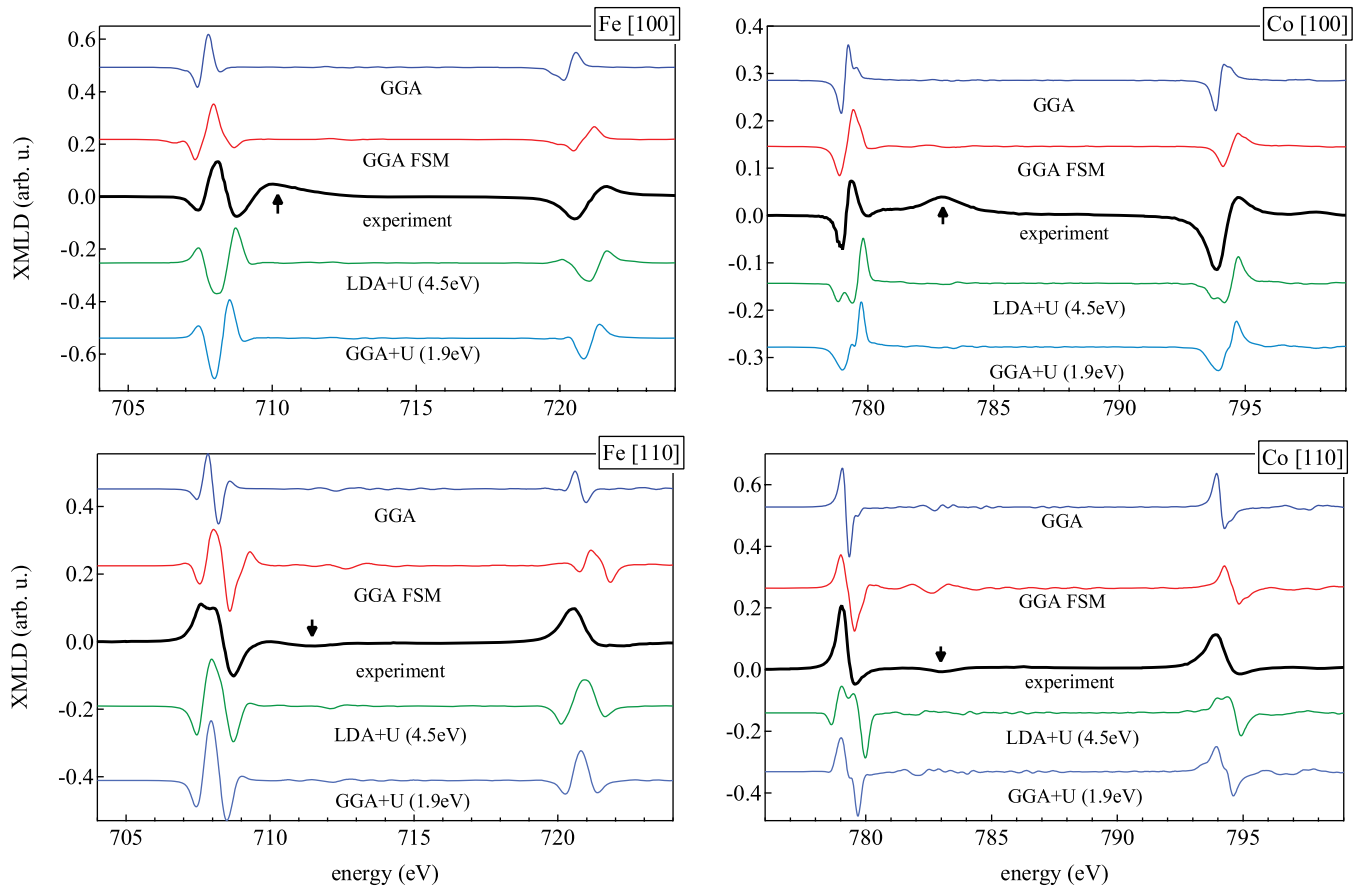


FIG. 5. (Color online) X-ray magnetic linear dichroism spectra calculated with different approaches, as discussed in the text. The theoretical spectra are vertically offset against the experimental spectra. They are aligned in energy and scaled to the experimental data.

than the values extracted with the white line sum rule (see Sec. IV B). However, they are larger than the theoretical hole numbers of the pure elements, which amount to 2.4 and 3.45, respectively.²³ Our values are close to the numbers of unoccupied d states of the free Co and Fe atoms. This atomiclike configuration could be the reason for the failure of the PBE functional to obtain the correct magnetic moment.

The calculated magnetic moments within the GGA FSM approach are $m_s^{\text{Co}} = 1.49 \mu_B$, $m_l^{\text{Co}} = 0.043 \mu_B$ and $m_s^{\text{Fe}} = 2.98 \mu_B$, $m_l^{\text{Fe}} = 0.043 \mu_B$. The interstitial contribution is almost zero. The calculated spin moment ratio is 2, which is smaller than the experimental value. The orbital moments are underestimated by a factor of about 2.3, which is typically observed in DFT calculations without orbital corrections.³¹

We note that it is still an open question why bulk magnetometry of presumably half-metallic Heusler compounds gives the integer Slater-Pauling values, which are only valid in the complete absence of valence-band spin-orbit coupling. XMCD does, however, always give small orbital moments, which should increase the total moment.

V. DISCUSSION

Kuneš *et al.* proposed a theoretical model of the XMLD, in which the XMLD is given as an energy derivative of differences

of the unoccupied e_g and t_{2g} densities of states:

$$\text{XMLD} \propto \Delta_x \frac{d}{dE} [\alpha(t_{2g\uparrow} - t_{2g\downarrow}) + \beta(e_{g\uparrow} - e_{g\downarrow})], \quad (1)$$

where Δ_x is the core-level exchange splitting, and α, β are constants, which take the values $\alpha = -1$ and $\beta = 2$ for the [100] magnetization direction.^{29,32} The energy dependence has been omitted for clarity. This model is only valid without spin-orbit coupling, which lifts the degeneracies of the crystal-field split doubly and triply degenerate d states. However, this model gives an instructive picture of the local crystal field sensitivity of the XMLD.

Consequently, the large differences observed for the GGA FSM and GGA+ U spectra along the [100] direction indicate significant changes in the distribution of the orbital symmetries (irreducible representations) of the d states.

In Fig. 6 we compare the total DOS of the GGA FSM calculation and the GGA+ U calculation neglecting spin-orbit coupling. The gap widths and positions of the Fermi levels are different, and the width of the unoccupied minority d states is larger in the GGA+ U calculation. The size of the minority gap in the GGA+ U calculation is about $U/2$. The GGA FSM density of states is essentially the same as that of a plain GGA calculation, with the majority and minority states being rigidly shifted against each other. Due to their overall

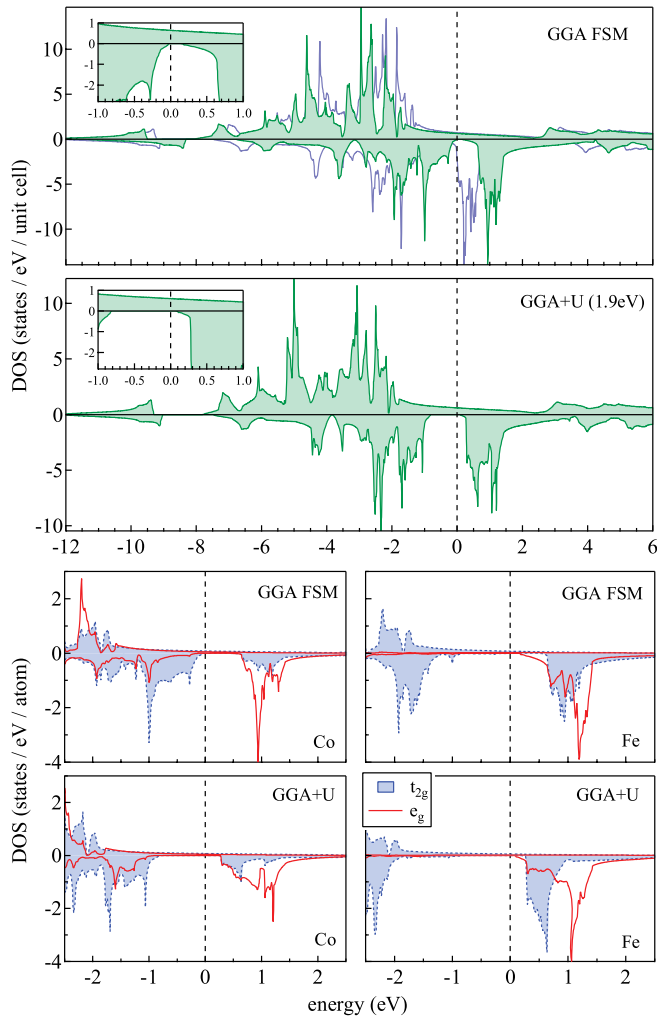


FIG. 6. (Color online) (Top) Total densities of states of Co_2FeSi with the GGA fixed spin moment (FSM) and GGA+ U (1.9 eV) approaches. The insets show the vicinity of the Fermi level. The light blue line in the top panel represents the GGA calculation. (Bottom) Partial densities of states of Co and Fe in the two computational approaches. The spectra are decomposed into the irreducible representations (e_g and t_{2g}) of the d states. Spin-orbit coupling is neglected.

similarity, typical experimental techniques that probe the DOS (photoemission, inverse photoemission, x-ray absorption) are hardly able to distinguish between the models of the electronic structure.

By decomposing the individual d projections into their orbital symmetries, we are able to observe differences between the GGA FSM and GGA+ U models. This is shown in the bottom part of Fig. 6. The DOS of the two orbital symmetries (e_g and t_{2g}) have entirely different structures in the two calculations. The e_g and t_{2g} states are more split in GGA+ U (i.e., the crystal field is stronger), and the hybridization between Co and Fe t_{2g} states becomes stronger as well. The Co e_g states are broader in GGA+ U , and the Fe t_{2g} states have a larger weight in GGA+ U than in GGA FSM. The crystal field splitting is the driving mechanism for the gap creation in the half-metallic Heusler compounds.¹ Obviously, the + U

operator (in the FLL formulation) enhances the crystal field splitting and forms the half-metallic gap.

It has been shown that the LDA+ U formalism can be derived as an approximation to the quasiparticle self-energy within the GW method.^{33,34} The derivation involves three assumptions: (1) the screened Coulomb interaction (described by U) is static; (2) only localized states are subject to the quasiparticle corrections; (3) the many-body exchange interaction between localized and itinerant electrons is neglected. Thus, LDA+ U is a kind of on-site Hartree-Fock theory with the effective screening given by the + U parameter. It does provide results that are quite similar to those from the hybrid PBE0 functional.³ The inclusion of Hartree-Fock exchange without the proper spacial and frequency dependence of the screening (i.e., the correlation) allows one to obtain the magnetic moment of Co_2FeSi correctly, but fails at the correct prediction of the unoccupied states' band structure.

The GGA is able to describe the wave functions and unoccupied states reasonably well up to a rigid shift of the latter. Since the GGA can be seen as a static, local, and orbital-independent approximation to the GW self-energy, the success of reproducing the XMLD spectra well is based on a cancellation of errors, due to omission of both the nonlocality and the frequency dependence in the exchange and correlation contributions. The good balance between exchange and correlation in the LDA (and GGA, which is essentially the same theory) has been confirmed earlier by Kotani and Grüning *et al.* These authors have performed calculations of transition metal and semiconductor band structures with the EXX + RPA approach, which treats exchange and correlation on the same level of many-body perturbation theory.^{35,36} EXX + RPA reproduced the LDA results well, including magnetic moments and exchange splittings of Fe, Co, and Ni. However, for MnO, where screening is weak, EXX + RPA gave substantial improvement of the band structure.³⁵ Furthermore, GW calculations on half-metallic CrAs and MnAs by Damewood and Fong³⁷ demonstrated that the GGA can predict half-metallic gaps that are very close to the GW values, depending on the details of the local fields and the associated screening.

The GGA FSM band structure has a small gap (about 0.1-eV wide) in the minority states, and the Fermi energy is located in the gap. Inclusion of spin-orbit coupling closes this small gap. This observation may explain the rather low TMR values of magnetic tunnel junctions with Co_2FeSi electrodes, the lack of half-metallic characteristics in the tunneling conductance curves, and the large Gilbert damping.¹⁰

VI. CONCLUSIONS

Our experimental results show that the features associated with the GGA+ U band structure are not present in Co_2FeSi . GGA+ U predicts an inadequate distribution of the crystal-field split d states, which we identified by x-ray magnetic linear dichroism. The + U operator opens a minority gap at the Fermi energy, which necessarily leads to an integer magnetic moment. While exchange and correlation effects beyond the GGA are certainly important for the description of Co_2FeSi , the simple + U approach does not produce the correct band structure. The PBE functional is able to produce

an unoccupied states' band structure for Co₂FeSi which is approximately correct up to a rigid shift of the minority *d* states.

Co₂FeSi is a complex material, being neither close to the electron gas (the GGA fails to find the correct ground-state magnetic moment), nor being strongly correlated (GGA+*U* fails at the description of spectral properties). That calls for further refinement of the approximations to the density functional. More flexible functional forms, such as meta-GGA functionals (adding information on the kinetic energy density), may perform better in this respect. Co₂FeSi is therefore an interesting test case for new density functionals. Ultimately, many-body approaches, such as EXX+RPA,³⁵ the *GW* approximation (possibly including some kind of self-consistency), or

DMFT^{38,39} might be required to obtain a consistent theoretical picture of Co₂FeSi.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from Bundesministerium für Bildung und Forschung (BMBF) and Deutsche Forschungsgemeinschaft [(DFG) Grant No. RE 1052/22]. They are grateful for the opportunity to work at the Advanced Light Source, Berkeley, CA, which is supported by the Director, Office of Science, Office of Basic Energy Sciences of the US Department of Energy under Contract No. DE-AC02-05CH11231. Special thanks go to the developers of the ELK code.

*meinert@physik.uni-bielefeld.de

¹I. Galanakis, P. H. Dederichs, and N. Papanikolaou, *Phys. Rev. B* **66**, 174429 (2002).

²S. Wurmehl, G. H. Fecher, H. C. Kandpal, V. Ksenofontov, C. Felser, H. J. Lin, and J. Morais, *Phys. Rev. B* **72**, 184434 (2005).

³A. Nourmohammadi and M. R. Abolhasani, *Solid State Commun.* **150**, 1501 (2010).

⁴B. Balke, G. H. Fecher, H. C. Kandpal, C. Felser, K. Kobayashi, E. Ikenaga, J. J. Kim, and S. Ueda, *Phys. Rev. B* **74**, 104405 (2006).

⁵H. C. Kandpal, G. H. Fecher, and C. Felser, *J. Phys. D: Appl. Phys.* **40**, 1507 (2007).

⁶M. Kumar, T. Nautiyal, and S. Auluck, *J. Phys.: Condens. Matter* **21**, 196003 (2009).

⁷M. Kim, H. Lim, and J. I. Lee, *Thin Solid Films* **519**, 8419 (2011).

⁸Y. Feng, B. Wu, H. K. Yuan, and H. Chen, *Applied Mechanics and Materials* **130–134**, 1430 (2012).

⁹W. C. Lim, G. M. Choi, T. D. Lee, and S. A. Seo, *IEEE Trans. Magn.* **40**, 2595 (2008).

¹⁰T. Kubota, S. Tsunegi, M. Oogane, S. Mizukami, T. Miyazaki, H. Naganuma, and Y. Ando, *Appl. Phys. Lett.* **94**, 122504 (2009).

¹¹C. G. F. Blum, C. A. Jenkins, J. Barth, C. Felser, S. Wurmehl, G. Friemel, C. Hess, G. Behr, B. Büchner, A. Reller, S. Riegg, S. G. Ebbinghaus, T. Ellis, P. J. Jacobs, J. T. Kohlhepp, and H. J. M. Swagten, *Appl. Phys. Lett.* **95**, 161903 (2009).

¹²M. Kallmayer, P. Klaer, H. Schneider, G. Jakob, H. J. Elmers, D. Legut, and P. M. Oppeneer, *Phys. Rev. B* **84**, 054448 (2011).

¹³M. Kallmayer, H. Schneider, G. Jakob, H. J. Elmers, B. Balke, and S. Cramm, *J. Phys. D: Appl. Phys.* **40**, 1552 (2007).

¹⁴<http://elk.sourceforge.net> Computer code ELK, Version 1.4.5.

¹⁵J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

¹⁶J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).

¹⁷A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, *Phys. Rev. B* **52**, 5467 (1995).

¹⁸K. Schwarz and P. Mohn, *J. Phys. F: Met. Phys.* **14**, L129 (1984).

¹⁹H. Rathgen and M. I. Katsnelson, *Phys. Scr., T* **109**, 170 (2004).

²⁰Y. Takamura, R. Nakane, and S. Sugahara, *J. Appl. Phys.* **105**, 07B109 (2009).

²¹H. Schneider, Ch. Herbort, G. Jakob, H. Adrian, S. Wurmehl, and C. Felser, *J. Phys. D: Appl. Phys.* **40**, 1548 (2007).

²²J. Stöhr, *J. Elec. Spec. Rel. Phen.* **75**, 253 (1995).

²³A. Scherz, Ph.D thesis, Freie Universität, Berlin.

²⁴E. Arenholz, G. van der Laan, R. V. Chopdekar, and Y. Suzuki, *Phys. Rev. B* **74**, 094407 (2006).

²⁵N. D. Telling, P. S. Keatley, G. van der Laan, R. J. Hicken, E. Arenholz, Y. Sakuraba, M. Oogane, Y. Ando, K. Takanashi, A. Sakuma, and T. Miyazaki, *Phys. Rev. B* **78**, 184438 (2008). Note that in this paper the magnetization directions are given with respect to the substrate.

²⁶M. Meinert, J. M. Schmalhorst, C. Klewe, G. Reiss, E. Arenholz, T. Böhnert, and K. Nielsch, *Phys. Rev. B* **84**, 132405 (2011).

²⁷M. Meinert, J. Schmalhorst, H. Wulfmeier, G. Reiss, E. Arenholz, T. Graf, and C. Felser, *Phys. Rev. B* **83**, 064412 (2011).

²⁸E. Arenholz, G. van der Laan, A. McClure, and Y. Idzerda, *Phys. Rev. B* **82**, 180405 (2010).

²⁹F. Nolting, D. Legut, J. Ruzs, P. M. Oppeneer, G. Woltersdorf, and C. H. Back, *Phys. Rev. B* **82**, 184415 (2010).

³⁰R. Laskowski and P. Blaha, *Phys. Rev. B* **82**, 205104 (2010).

³¹O. Šipr, J. Minár, A. Scherz, H. Wende, and H. Ebert, *Phys. Rev. B* **84**, 115102 (2011).

³²J. Kuneš and P. M. Oppeneer, *Phys. Rev. B* **67**, 024431 (2003).

³³V. I. Anisimov, F. Aryasetiawan, and A. I. Liechtenstein, *J. Phys.: Condens. Matter* **9**, 767 (1997).

³⁴H. Jiang, R. I. Gomez-Abal, P. Rinke, and M. Scheffler, *Phys. Rev. B* **82**, 045108 (2010).

³⁵T. Kotani, *J. Phys.: Condens. Matter* **10**, 9241 (1998).

³⁶M. Grüning, A. Marini, and A. Rubio, *J. Chem. Phys.* **124**, 154108 (2006).

³⁷L. Damewood and C. Y. Fong, *Phys. Rev. B* **83**, 113102 (2011).

³⁸J. Minár, *J. Phys.: Condens. Matter* **23**, 253201 (2011).

³⁹S. Biermann, F. Aryasetiawan, and A. Georges, *Phys. Rev. Lett.* **90**, 086402 (2003).