



Structural characterization of the Co_2FeZ ($Z = \text{Al}, \text{Si}, \text{Ga}, \text{and Ge}$) Heusler compounds by x-ray diffraction and extended x-ray absorption fine structure spectroscopy

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Structural characterization of the Co_2FeZ ($Z=\text{Al, Si, Ga, and Ge}$) Heusler compounds by x-ray diffraction and extended x-ray absorption fine structure spectroscopy

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This work reports on the structure of Fe containing, Co_2 -based Heusler compounds that are suitable for magnetoelectronic applications. The compounds Co_2FeZ (where $Z=\text{Al, Si, Ga, and Ge}$) were investigated using the x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS) techniques. Using XRD, it was shown conclusively that Co_2FeAl crystallizes in the $B2$ structure whereas Co_2FeSi crystallizes in the $L2_1$ structure. For compounds containing Ga or Ge, the XRD technique cannot be used to easily distinguish between the two structures. For this reason, the EXAFS technique was used to elucidate the structure of these two compounds. Analysis of the EXAFS data indicated that both compounds crystallize in the $L2_1$ structure. © 2007 American Institute of Physics. [DOI: 10.1063/1.2731314]

Heusler compounds have been recognized as suitable materials for magneto-electronics.¹ The Co_2 -based compounds are of special interest for applications as they exhibit a wide range of magnetic properties with magnetic moments up to $1.5\mu_B$ per atom and Curie temperatures up to 1100 K.² In particular, the compounds based on Co_2 and Fe are presently used in tunneling magnetoresistive (TMR) devices.³⁻⁷ In most of the cases, compounds with Al or Si as main group element are used.

Studies of the Co_2FeZ compounds with Ga or Ge on the Z position are mostly reported for bulk samples rather than for thin films. Bulk Co_2FeSi has been reported by Niculescu *et al.*⁸ and was investigated in detail by Wurmehl *et al.*^{2,9} Co_2FeGa and Co_2FeGe have been reported by Bushow *et al.*¹⁰ to exist in the $L2_1$ structure. In many cases, when the main group element is from the same period of the periodic system as the transition metals, x-ray or neutron diffraction does not provide enough information to determine the correct structure unambiguously. The correct $L2_1$ structure, however, is a necessary requirement for a high spin polarization of the materials as base for a high TMR ratio.¹

Therefore, additional methods are needed to explore the correct structure. Particularly, extended x-ray absorption fine structure (EXAFS) and Mössbauer spectroscopy can provide additional information about the short range order of the structure.¹¹

The feasibility of using EXAFS for structural investigations of Heusler compounds was demonstrated by Ravel *et al.*¹² for the example Co_2MnSi . Therefore, the present work reports on the structural investigation of Co_2FeZ ($Z=\text{Al, Si, Ga, and Ge}$) Heusler compounds using a combination of x-ray diffraction (XRD) and EXAFS.

The Co_2FeZ samples with $Z=\text{Al, Si, Ga, and Ge}$ have been prepared by arc melting with consecutive postannealing

(for details see, e.g., Ref. 9). The long range order of the samples has been investigated by means of x-ray powder diffraction. The powder samples have been investigated using $\text{Mo } K\alpha$ radiation. The measured diffraction data were refined using the Rietveld method. The lattice parameters determined for the four compounds are reported in Table I.

Figure 1 displays the powder diffraction pattern of the four compounds. The shift of the most pronounced reflection at about 20° is due to the different lattice parameters of the four compounds. Typical for the $L2_1$ structure is the occurrence of the (111) and (200) reflections as seen in the powder pattern of Co_2FeSi . Obviously, the (200) reflex is absent in the diffraction pattern of Co_2FeAl , as is typical for the $B2$ structure [simple cubic (sc), CsCl-like]. Both fcc-type reflections, typical of the $L2_1$ structure, are missing in the pattern of Co_2FeGa and Co_2FeGe . The absence of those reflections might indicate an $A2$ (bcc) structure. However, in the present case it may also be caused by the nearly equal scattering factors of Co, Fe, and the Z element (Ga, Ge) that are all from the same period. For those two compounds, indeed, the R -factor analysis resulted in nearly equal values independent whether an $A2$, $B2$, or $L2_1$ structure model was assumed in

TABLE I. Lattice parameter and calculated, relative XRD intensities for Co_2FeZ with $Z=\text{Al, Si, Ga, Ge}$. The intensities have been calculated for excitation by $\text{Cu } K\alpha$ and $\text{Mo } K\alpha$ radiations. The relative intensities are given in percentage a is the lattice parameter extracted from the Rietveld refinement.

Compound	a [Å]	I_{111}/I_{220}		I_{200}/I_{220}	
		$\text{Cu } K\alpha$	$\text{Mo } K\alpha$	$\text{Cu } K\alpha$	$\text{Mo } K\alpha$
Co_2FeAl	5.737	6.4	5.7	4.6	5.2
Co_2FeSi	5.64	5.7	5.0	4.2	3.8
Co_2FeGa	5.751	0.8	0.7	0.1	0.1
Co_2FeGe	5.743	0.9	0.9	0.2	0.2

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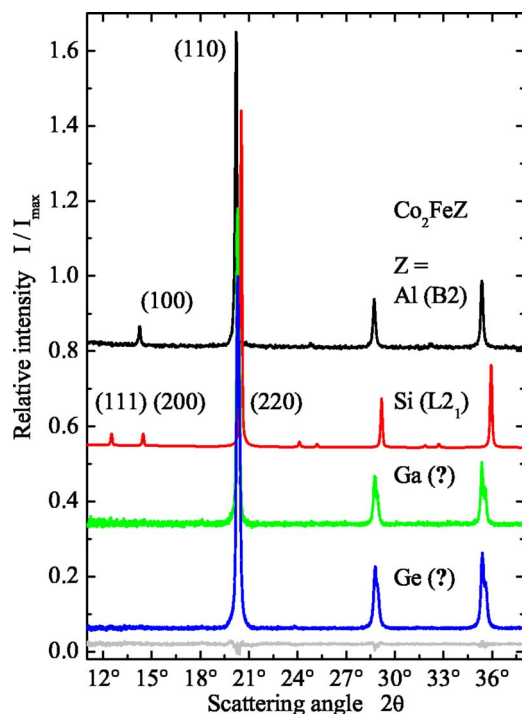


FIG. 1. (Color online) XRD of Co_2FeZ with $Z=\text{Al, Si, Ga, Ge}$. The XRD pattern have been excited by $\text{Mo } K_\alpha$ radiation. Note the different indexing of the reflections in the sc ($Z=\text{Al}$) and fcc ($Z=\text{Si}$) crystal systems. The line below $Z=\text{Ge}$ is the difference between the measured data and the $L2_1$ Rietveld refinement for Co_2FeGe .

the Rietveld refinement. Figure 1 displays additionally the difference between Rietveld refinement and measured data for Co_2FeGe assuming the $L2_1$ structure, as an example. This demonstrates that the fcc-type reflections cannot be detected under the experimental conditions.

A rough estimation of the relative intensities of the (111) and (200) reflections is summarized in Table I. The relative peak heights for the fcc-typical reflections have been calculated for typical laboratory x-ray sources using Cu or Mo anodes. The decrease of the reflex intensities by about one order of magnitude in the Ga and Ge containing compounds, compared to Al or Si, is remarkable.

The EXAFS measurements have been performed at the XAFS1 beamline of the Brazilian Synchrotron Light Laboratory using a Si (111) channel-cut monochromator. The spectra have been collected at the Fe (7112 eV) and Co (7709 eV) K edges at room temperature in the transmission mode using three ionization chambers. Co or Fe standard foils were placed at the third chamber in order to check the monochromator energy calibration. The EXAFS spectra were analyzed using the IFEFFIT analysis package.¹³ The isolated-atom background function was removed from the experimental x-ray absorption coefficient data yielding the $\chi(k)$ signal. The Fourier transform was applied using a Hanning window with a k value of 8 \AA^{-1} . The structural parameters were obtained from a least-squares fit to the data in r and k space using phase shift and amplitudes obtained from the FEFF code¹⁴ calculated for Co_2FeAl in the $B2$ and $L2_1$ structures and for Co_2FeSi , Co_2FeGa , and Co_2FeGe in the $L2_1$ structure. The results are summarized in Figs. 2 and 3.

The EXAFS signals at the Fe and Co [Figs. 2(a) and 3(a)] K edges display the characteristic pattern of a cubic structure. At both edges, the EXAFS signals for the alloys

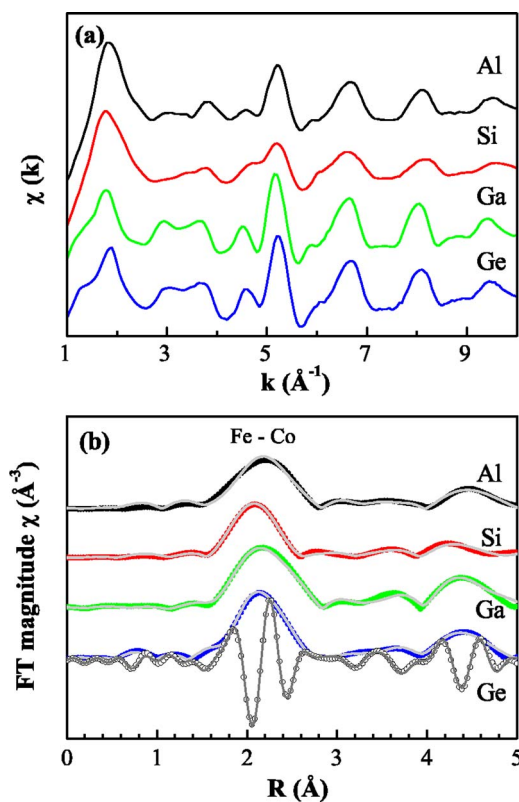


FIG. 2. (Color online) EXAFS at the Fe K edges of Co_2FeZ with $Z=\text{Al, Si, Ga, Ge}$. (a) EXAFS oscillations extracted from the x-ray absorption measurements at the Fe K edge. (b) Corresponding Fourier transforms (symbols) and best fitting results (gray line). The imaginary part of the Fourier transform is displayed for the Co_2FeGe compound (open circles).

containing the lighter Z elements (Al and Si) are more attenuated due to the lower backscattering amplitudes of these elements, compared to the Ga and Ge ones. The fitting of the Fourier transforms are displayed in part (b) of Figs. 2 and 3. The imaginary part is displayed for the Co_2FeGe in order to exemplarily demonstrate the typical fine quality of the fittings achieved.

The best fittings were obtained considering that Co_2FeAl assumes the $B2$ structure and all others (Co_2FeSi , Co_2FeGa , and Co_2FeGe) are ordered in the $L2_1$ structure. An excellent agreement between the data and theory was accomplished as demonstrated in Figs. 2 and 3 as well as by the low R -factor values (between 0.01 and 0.03).

The Fourier transforms at the Fe K -edge spectra (Fig. 3) of all samples exhibit two well defined peaks at about 2.2 and 4.5 Å (uncorrected for the phase shift), that correspond to the Fe–Co contribution in the coordination shell and Fe–Fe contribution, respectively. The Fe– Z ($Z=\text{Al, Si, Ga, and Ge}$) and multiple scattering contributions appear in the quite smooth region between the two main peaks. This is consistent to the coordination shell of Fe on the cubic environment composed of eight Co atoms. On the other hand each Co atom is surrounded by four Fe atoms and four Z (Al, Si, Ga, and Ge) atoms.

As a result, the Fourier transforms of the Co edge spectra (Fig. 2) for the Co_2FeAl and Co_2FeSi display a splitting of the first peak due to the Co bond with the lighter atom (Al and Si) and Co–Fe bond in the coordination shell. For Co_2FeGa and Co_2FeGe , a well defined first peak is attributed to the superposition of Co–Fe and Co– Z contributions ($Z=\text{Ga and Ge, respectively}$). The presence of heavier atoms,

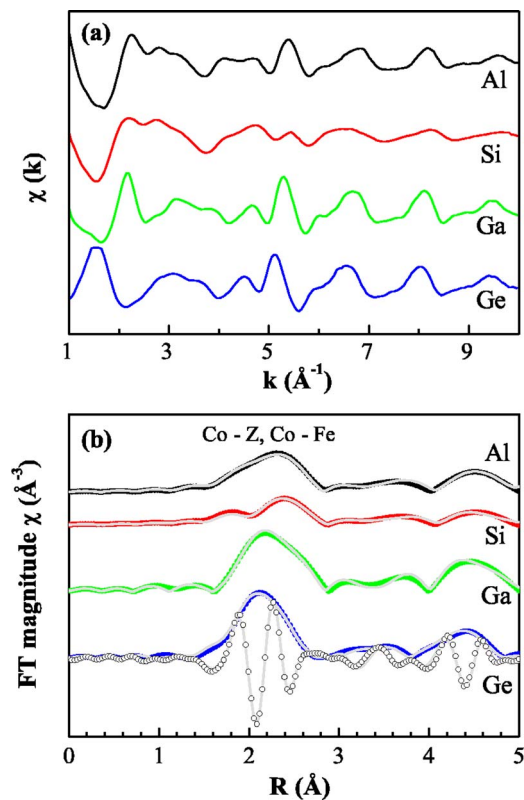


FIG. 3. (Color online) EXAFS at the Co K edges of Co_2FeZ with $Z=\text{Al, Si, Ga, Ge}$. (a) EXAFS oscillations extracted from the x-ray absorption measurements at the Co K edge. (b) Corresponding Fourier transforms (symbols) and best fitting results (gray line). The imaginary part of the Fourier transform is displayed for the Co_2FeGe compound (open circles).

and consequently higher backscattering amplitudes, results in more intense peaks as compared to the previous alloys. A next more pronounced peak appears for all samples at about 4.5 \AA and corresponds to the Co–Co contribution.

The overall fitting procedures of all Co_2FeZ alloys lead to physically reasonable numbers close to the theoretical structural models. The obtained values for the passive electron reduction factor (S_0^2) were in the range of 0.8–1.0. The Debye-Waller factor (σ^2) values for the different paths were throughout small, ranging from 0.007 to 0.01. The shifts in distances (ΔR) were also small, and the typical variation was -0.02 to -0.06 \AA .

Taking the results from the Fe and the Co K edges together, EXAFS gives a clear indication for the $L2_1$ structure in the compounds with $Z=\text{Ga}$ and Ge . This becomes also evident in the comparison to the results from the compounds with Al and Si that clearly adopt the $B2$ and $L2_1$ structures, respectively.

In summary, it has been demonstrated that EXAFS of Heusler compounds is a suitable method for structural investigations. It is particularly useful if x-ray diffraction gives ambiguous results about the correct structure. It is expected that EXAFS may also help for a better understanding of the structure of thin films in order to improve the quality of TMR junctions.

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