Structural characterization of the Co$_2$FeZ (Z = Al, Si, Ga, and Ge) Heusler compounds by x-ray diffraction and extended x-ray absorption fine structure spectroscopy

Benjamin Balke, Sabine Wurmehl, Gerhard H. Fecher, Claudia Felser, Maria C. M. Alves, Fabiano Bernardi, and Jonder Morais

Citation: Applied Physics Letters 90, 172501 (2007); doi: 10.1063/1.2731314
View online: http://dx.doi.org/10.1063/1.2731314
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/90/17?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Quantitative analysis of anisotropic magnetoresistance in Co2MnZ and Co2FeZ epitaxial thin films: A facile way to investigate spin-polarization in half-metallic Heusler compounds

Phase stability of Heusler compound Co2FeSi under pressure: An in-situ x-ray diffraction investigation
J. Appl. Phys. 110, 083523 (2011); 10.1063/1.3656983

Influence of mixing the low-valent transition metal atoms (Y, Y' = Cr, Mn, Fe) on the properties of the quaternary Co$_2$(Y$_{1-x}$Y'$_x$)Z (Z = Al, Ga, Si, Ge, or Sn) Heusler compounds

Differentiation of biological hydroxyapatite compounds by infrared spectroscopy, x-ray diffraction and extended x-ray absorption fine structure
J. Appl. Phys. 90, 6440 (2001); 10.1063/1.1408267

Redistribution of Zr and Ga in Nd$_2$Fe$_{14}$B-based magnets during the hydrogen disproportionation desorption recombination process: An x-ray absorption fine structure study
J. Appl. Phys. 85, 5681 (1999); 10.1063/1.369839
Structural characterization of the Co$_2$FeZ (Z=Al, Si, Ga, and Ge) Heusler compounds by x-ray diffraction and extended x-ray absorption fine structure spectroscopy

Benjamin Balke, Sabine Wurmehl, Gerhard H. Fecher, and Claudia Felser

Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, 55099 Mainz, Germany

Maria C. M. Alves, Fabiano Bernardi, and Jonder Morais

Instituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, Rio Grande do Sul 91501-970, Brazil and Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre, Rio Grande do Sul 91501-970, Brazil

(Received 19 February 2007; accepted 24 March 2007; published online 23 April 2007)

This work reports on the structure of Fe containing, Co$_2$-based Heusler compounds that are suitable for magneto-electronic applications. The compounds Co$_2$FeZ (where Z=Al, Si, Ga, and Ge) were investigated using the x-ray diffraction (XRD) and extended x-ray absorption fine structure techniques. Using XRD, it was shown conclusively that Co$_2$FeAl crystallizes in the B$_2$ structure whereas Co$_2$FeSi crystallizes in the L$_2_1$ 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 L$_2_1$ structure. © 2007 American Institute of Physics. [DOI: 10.1063/1.2731314]

Heusler compounds have been recognized as suitable materials for magneto-electronics. 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 1.5μ$_B$/atom and Curie temperatures up to 1100 K. In particular, the compounds based on Co$_2$ and Fe are presently used in tunneling magnetoresistive (TMR) devices. In most of the cases, compounds with Al or Si as main group element are used.

Studies of the Co$_2$FeZ compounds with Ga or Ge on the Z positions are mostly reported for bulk samples rather than for thin films. Bulk Co$_2$FeSi has been reported by Niculescu et al. and was investigated in detail by Wurmehl et al. Co$_2$FeGa and Co$_2$FeGe have been reported by Bushow et al. to exist in the L$_2_1$ structure. In many cases, when the main group element is from the same period of the periodic system the x-ray or neutron diffraction does not provide enough information to determine the correct structure unambiguously. The correct L$_2_1$ structure, however, is a necessary requirement for a high spin polarization of the materials as base for a high TMR ratio.

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.

The feasibility of using EXAFS for structural investigations of Heusler compounds was demonstrated by Ravel et al. for the example Co$_2$MnSi. Therefore, the present work reports on the structural investigation of Co$_2$FeZ (Z=Al, Si, Ga, and Ge) Heusler compounds using a combination of x-ray diffraction (XRD) and EXAFS.

The Co$_2$FeZ samples with Z=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 Mo Kα 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 L$_2_1$ structure is the occurrence of the (111) and (200) reflections as seen in the powder pattern of Co$_2$FeSi. Obviously, the (200) reflex is absent in the diffraction pattern of Co$_2$FeAl, as is typical for the B$_2$ structure [simple cubic (sc), CsCl-like]. Both fcc-type reflections, typical of the L$_2_1$ structure, are missing in the pattern of Co$_2$FeGa and Co$_2$FeGe. The absence of those reflections might indicate an A$_2$ (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 A$_2$, B$_2$, or L$_2_1$ structure model was assumed in

<table>
<thead>
<tr>
<th>Compound</th>
<th>a [Å]</th>
<th>I$<em>{111}$/I$</em>{220}$</th>
<th>I$<em>{200}$/I$</em>{220}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_2$FeAl</td>
<td>5.737</td>
<td>6.4</td>
<td>5.7</td>
</tr>
<tr>
<td>Co$_2$FeSi</td>
<td>5.64</td>
<td>5.7</td>
<td>5.0</td>
</tr>
<tr>
<td>Co$_2$FeGa</td>
<td>5.751</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Co$_2$FeGe</td>
<td>5.743</td>
<td>0.9</td>
<td>0.9</td>
</tr>
</tbody>
</table>

*Electronic mail: felser@uni-mainz.de*
the Rietveld refinement. Figure 1 displays additionally the difference between Rietveld refinement and measured data for Co$_2$FeGe 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. 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 Å$^{-1}$. 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 code calculated for Co$_2$FeAl in the B2 and L2$_1$ structures and for Co$_2$FeSi, Co$_2$FeGa, and Co$_2$FeGe 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 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 of the Fourier transform is displayed for the Co$_2$FeGe compound (open circles).

As a result, the Fourier transforms of the Co 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 ($Z$=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.

FIG. 2. (Color online) EXAFS at the Fe K edges of Co$_2$FeZ with $Z$=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$_2$FeGe compound (open circles).
The obtained values for the passive electron reduction factor ($\Delta S^2$) were in the range of 0.8–1.0. The Debye-Waller factor ($\sigma^2$) values for the different paths were throughout small, ranging from 0.007 to 0.01. The shifts in distances ($\Delta R$) were also small, and the typical variation was $-0.02$ to $-0.06$ Å.

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 $Z=$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.

Financial support by DFG (research unit FG 559), DAAD (D06/33952), and CAPES PROBRAL (167/04) is gratefully acknowledged. Further support of this work was provided by CNPq (CT-Energ) and by the Brazilian Synchrotron Light Laboratory (LNLS) under proposal D04B-XAFS1-3304. The authors thank Gustavo Azevedo (LNLS, Campinas) for help with the experiments.

FIG. 3. (Color online) EXAFS at the Co $K$ edges of Co$_2$FeZ with $Z=$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$_2$FeGe compound (open circles).